

University of New Orleans

ScholarWorks@UNO

University of New Orleans Theses and
Dissertations

Dissertations and Theses

12-17-2004

Synthetic, Structural and Thermochemical Studies of N-Heterocyclic Carbene (NHC) and Tertiary Phosphine Ligands in the $\text{Ni}(\text{CO})_2(\text{L})_x$ (L-PR₃, NHC) Systems

Parisa Mahjoor
University of New Orleans

Follow this and additional works at: <https://scholarworks.uno.edu/td>

Recommended Citation

Mahjoor, Parisa, "Synthetic, Structural and Thermochemical Studies of N-Heterocyclic Carbene (NHC) and Tertiary Phosphine Ligands in the $\text{Ni}(\text{CO})_2(\text{L})_x$ (L-PR₃, NHC) Systems" (2004). *University of New Orleans Theses and Dissertations*. 190.

<https://scholarworks.uno.edu/td/190>

This Thesis is protected by copyright and/or related rights. It has been brought to you by ScholarWorks@UNO with permission from the rights-holder(s). You are free to use this Thesis in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you need to obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/or on the work itself.

This Thesis has been accepted for inclusion in University of New Orleans Theses and Dissertations by an authorized administrator of ScholarWorks@UNO. For more information, please contact scholarworks@uno.edu.

SYNTHETIC, STRUCTURAL AND THERMOCHEMICAL STUDIES OF *N*-
HETEROCYCLIC CARBENE (NHC) AND TERTIARY PHOSPHINE LIGANDS IN THE
 $\text{Ni}(\text{CO})_2(\text{L})_2$ ($\text{L} = \text{PR}_3, \text{NHC}$) SYSTEMS

A Thesis

Submitted to the Graduate Faculty of the
University of New Orleans
in partial fulfillment of the
requirements for the degree of

Master of Science
in
The Department of Chemistry

by

Parisa Mahjoor

B.Sc. (Hons) Chemistry, Shiraz University, 2001

December 2004

Copyright 2004, Parisa Mahjoor

To my Family, for their love and support

ACKNOWLEDGMENT

I would like to express my gratitude to my research advisor Professor Steven P. Nolan for his guidance and support during this period of my research.

The National Science Foundation is gratefully acknowledged for financial support of this work. Dr. Kenneth Moloy and DuPont CR&D are especially thanked for the gift of Ni(CO)_4 , as are Dr. Emilio Bunel and Eli Lilly and Co. for a generous donation of amines.

My committee members, Profs. Bruce C. Gibb, and John Wiley, are gratefully acknowledged.

I wish to thank Prof. Edwin D. Stevens for solving crystal structures for us.

Finally, I thank all my friends and co-workers : Renee Olano, Sandra Lochhead, Harneet Kaur, Rohit Singh, Roy Kelly, Oscar Navarro, Pierre deFromont and Drs. Fabiano Kauer, Reto Dorta, Natalie Scott and Mihai S. Viciu.

TABLE OF CONTENTS

List of Tables	vii
List of Schemes	viii
List of Figures	ix
Abstract	x
 Chapter 1. Nickel-Phosphine Complexes.....	1
1.1. Introduction.....	1
1.2. Ni-P Bond Energies	2
1.3. <i>N</i> -Heterocyclic Carbenes as Ancillary Ligands.....	5
1.3.1 Structure and Fundamental Characteristics	6
1.3.2 Synthesis of <i>N</i> -Heterocyclic Carbenes.....	7
1.4. Calorimetric Studies.....	9
1.5. Metal-Carbene Complexes.....	9
1.5.1 Nickel Complexes of <i>N</i> -Heterocyclic Carbenes	10
1.5.2 Ni-NHC Bond Energies	11
1.6. References and Notes.....	13
 Chapter 2. Synthetic, Structural and Thermochemical Studies of <i>N</i> -Heterocyclic Carbene (NHC) and Tertiary Phosphine Ligands in the Ni(CO) ₂ (L) ₂ (L = PR ₃ , NHC) Systems....	18
2.1. Introduction.....	18

2.2.	Results and Discussions.....	19
2.2.1	Synthesis and Structure Determination of Ni(CO) ₂ (ICy) ₂ and Ni(CO) ₂ (IMes) ₂	19
2.2.2	Calorimetric Studies.....	26
2.2.3	Absolute Ni-NHC and Ni-P Bond Enthalpies	29
2.3.	Conclusions.....	32
2.4.	Experimental Section.....	32
2.5.	References and Notes.....	36
	Chapter 3. Summary	40
	Appendices.....	41
	Appendix A: XRD Tables for Ni(CO) ₂ (ICy) ₂	41
	Appendix B: XRD Tables for Ni(CO) ₂ (IMes) ₂	56
	Vita.....	66

LIST OF TABLES

Chapter 1

Table 1.1.	Degree of Substitution of CO from Ni(CO) ₄ by Various Phosphorous Ligands Based on IR Intensities	3
Table 1.2.	Enthalpies for the Reaction of L (L = PR ₃) with Ni(COD) ₂ in Toluene at 25° C.....	5

Chapter 2

Table 2.1.	Crystallographic Data for Compounds Ni(CO) ₂ (NHC) ₂	24
Table 2.2.	Selected Bond Lengths (Å) and Bond Angles (deg) for Ni(CO) ₂ (NHC) ₂ Complexes.....	25
Table 2.3.	Selected Bond Lengths (Å) in Carbonylnickel-Carbene Complexes	26
Table 2.4.	Enthalpies of Ligand Substitution Reaction (kcal/mol) of Ni(CO) ₂ (I ^t Bu) and L [L = NHC (ICy, IMes), PR ₃ (PCy ₃ , P(<i>p</i> -toly) ₃ , P(<i>m</i> -toly) ₃ , PPh ₃)] ..	28
Table 2.5.	Enthalpies of Ligand Substitution Reaction (kcal/mol) of Ni(CO) ₂ (IAd) and L [L = NHC (ICy, IMes), PR ₃ (PCy ₃ , P(<i>p</i> -toly) ₃ , P(<i>m</i> -toly) ₃ , PPh ₃)] ..	28
Table 2.6.	Bond Dissociation Energies of Ni-NHC and Ni-P	30

LIST OF SCHEMES

Chapter 1

Scheme 1.1.	Substitution Reactions of $\text{Ni}(\text{COD})_2$ and L ($\text{L} = \text{PR}_3$)	4
Scheme 1.2.	Synthesis of Imidazolium Salts and Generation of Free Carbene	8
Scheme 1.3.	Liquid Ammonia Route	8
Scheme 1.4.	Enthalpies of Substitution (kcal/mol) for the reaction of $[\text{cp}^*\text{RuCl}]_4$ and L ($\text{L} = \text{ICy}, \text{IAd}, \text{IMes}, \text{PCy}_3, \text{P}^i\text{Pr}_3$).....	10
Scheme 1.5.	Substitution Reactions of $\text{Ni}(\text{CO})_4$ and (N, N'-bis(methylimidazol)-2-ylidene).....	11
Scheme 1.6.	Substitution Reactions of $\text{Ni}(\text{CO})_4$ and NHCs.....	12

Chapter 2

Scheme 2.1.	Synthesis of Complexs $\text{Ni}(\text{CO})_2(\text{Icy})_2$ (8) and $\text{Ni}(\text{CO})_2(\text{IMes})_2$ (9).....	20
Scheme 2.2.	Substitution Reactions of $\text{Ni}(\text{CO})_2(\text{NHC})$	27
Scheme 2.3.	Substitution Reaction of $\text{Ni}(\text{CO})_2(\text{I}^t\text{Bu})$	30

LIST OF FIGURES

Chapter 1

Figure 1.1.	Nucleophilic <i>N</i> -Heterocyclic Carbenes.....	6
Figure 1.2.	Common Saturated and Unsaturated <i>N</i> -Heterocyclic Carbenes.....	7

Chapter 2

Figure 2.1.	Ball and Stick Structure of $\text{Ni}(\text{CO})_2(\text{ICy})_2$ (8)	21
Figure 2.2.	Ball and Stick Structure of $\text{Ni}(\text{CO})_2(\text{IMes})_2$ (9)	22

ABSTRACT

Carbonyl complexes of Ni(0) incorporating two *N*-heterocyclic carbenes of the type Ni(CO)₂(NHC)₂ (NHC = ICy [*N,N'*-bis(cyclohexylimidazol)-2-ylidene], IMes [*N,N'*-bis(2,4,6-trimethylphenyl)-imidazol)-2-ylidene]) have been prepared. The complexes Ni(CO)₂(ICy)₂ (**8**) and Ni(CO)₂(IMes)₂ (**9**) have been synthesized and characterized by single crystal X-ray diffraction. The enthalpy of substitution reactions of Ni(CO)₂(NHC) (NHC = I^tBu [*N,N'*-bis(*tert*-butylimidazol)-2-ylidene], IAd [*N,N'*-bis(1-adamentylimidazol)-2-ylidene]) with NHC and tertiary phosphine ligands leading to the formation of Ni(CO)₂(L)₂ (L = NHC, PR₃) complexes have been determined. The solution calorimetric investigations reiterate the greater electron donating property of the NHC ligands compared to tertiary phosphines. Thermochemical studies of the substitution reactions of Ni(CO)₂(NHC) (NHC = I^tBu, IAd) forming complexes (**8**) and (**9**) led to the determination of average bond dissociation energy of Ni-NHC (NHC = ICy, IMes) and Ni-P (P = PCy₃, PPh₃, P(*p*-Tol)₃, P(*m*-Tol)₃).

CHAPTER 1

Nickel-Phosphine Complexes

1.1 Introduction

Since the discovery of $\text{Ni}(\text{PCl}_3)_4$ ¹ and $\text{Ni}(\text{PF}_3)_4$ ² in 1951, a variety of zerovalent nickel complexes with phosphorus ligands have been discovered.³ However, Tolman was the first to investigate the effect of steric and electronic of the phosphorus ligands in $\text{Ni}(0)$ complexes.^{4,5} It had been known that replacement of one or more CO's of a transition metal carbonyl with tertiary phosphine ligands cause the CO stretching frequencies of the remaining carbonyls to fall, by an amount depending on the number and nature of the phosphorous ligands.⁶⁻¹¹ In 1970, Tolman applied this basic principle to determine the electron donor-acceptor property of a series of tertiary phosphine ligands based on the A_1 carbonyl stretching of $\text{Ni}(\text{CO})_3\text{L}$ ($\text{L} = \text{PR}_3$) complexes in CH_2Cl_2 .⁵ He clarified that ν_{co} A_1 depends on the electronic nature of the phosphorus ligands. The greater the electron density on the metal (and the greater the charge), the greater the back bonding to CO, and the lower the energy of the carbonyl stretching vibration. Therefore, the nickel in $\text{Ni}(\text{CO})_3\text{L}$ ($\text{L} = \text{P}(t\text{-But})_3$) carries the greatest electron density; it is the most able to donate electron density to π^* orbital of the carbonyl ligand; consequently, the

carbonyl ligands in $\text{Ni(CO)}_3\text{L}$ ($\text{L} = \text{P}(t\text{-Bu})_3$) have the weakest C-O bonds and the lowest energy stretching bonds. However, as a consequence of highly electropositive fluorine PF_3 , was found to be the weakest donor ($\nu_{\text{CO}} A_1 = 2110.8\text{cm}^{-1}$).

The steric effects of phosphorous ligands was investigated by a series of ligand exchange reactions of Ni(CO)_4 and tertiary phosphine ligands of different bulk.⁴ The results showed that the degree of substitution of CO from Ni(CO)_4 by various tertiary phosphine ligands, depends on the size of the phosphorous ligands rather than their electronic character (Table 1.1).⁴

1.2 Ni-P Bond Energies

The first Ni-P bond energy was reported by Connor and co-workers in 1974.¹² They interpreted the electron impact-mass spectroscopic studies by Kiser and Clark¹³ on $\text{Ni(PF}_3)_4$ to yield a value of 43 kcal/mol for the average strength of the Ni- PF_3 bonds. In 1977, Tolman carried out a calorimetric study of the reactions of various phosphorus ligands (and $t\text{-BuNC}$) with Ni(COD)_2 (COD = 1,5-cyclooctadienenickel) in which the steric and electronic effects of phosphorous ligands were investigated.¹⁴

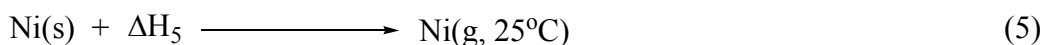
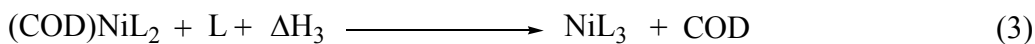
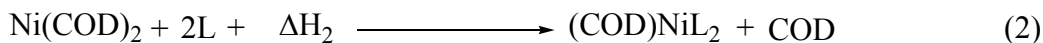
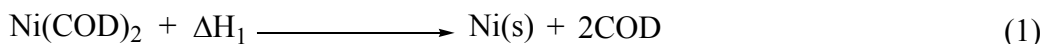
Table 1.1. Degree of Substitution of CO From Ni(CO)₄ by Various Phosphorous Ligands Based on IR Intensities

Ligand	Estimated Degree of Substitution	Ligand Cone Angle, (deg)
P(OCH ₂) ₃ CCH ₃	3.7	101 ± 2
P(OCH ₃) ₃	3.0	107 ± 2
P(OC ₆ H ₅) ₃	2.7	121 ± 10
P(CH ₃) ₃	2.4	118 ± 4
P(C ₄ H ₉) ₃	2.2	130 ± 4
P(C ₆ H ₅) ₃	2.0	145 ± 2
P(<i>i</i> -C ₃ H ₇) ₃	1.7	160 ± 10
P(C ₆ H ₁₁) ₃	1.5	179 ± 10
P(<i>t</i> -C ₄ H ₉) ₃	1.0	182 ± 2
P(C ₆ F ₅) ₃	0.3	184 ± 2

The reaction of Ni(COD)₂ with L (L = PR₃) occurs in three stages, represented by eq 2-4 (Scheme 1.1). With large ligands such as PPh₃, reaction stops with eq 2 or eq 3. However, with small phosphorus ligands such as PEt₃ the reaction stops with eq 4 (Table 1. 2).¹⁴

Having the enthalpy change ($\Delta H = -3$ kcal/mol) for the decomposition of Ni(COD)₂ (eq 1) and the known heat of vaporization of metallic nickel ($\Delta H_5 = 101.6$ kcal/mol)¹⁵ (eq 5), the mean Ni-P bond energies were determined based on equation 6 and 7 (Scheme 1.1).

Scheme 1.1. Substitution Reactions of Ni(COD)₂ and L (L = PR₃)



$$\text{For NiL}_4 : 4\text{D(Ni-P)} = \Delta H_5 + \Delta H_1 - (\Delta H_2 + \Delta H_3 + \Delta H_4) \quad (6)$$

$$\text{For NiL}_3 : 3\text{D(Ni-P)} = \Delta H_5 + \Delta H_1 - (\Delta H_2 + \Delta H_3) \quad (7)$$

Comparison of the Ni-P bond energies (Table 1.2) showed that D(Ni-P) is not strongly dependent on the electron donor-acceptor characteristic of the phosphorus ligands. It was clarified that the decreasing electrothermicity in the formation of NiL₄ (L = PR₃) complexes is largely due to increased steric strain energy in complexes with bulkier L (L = PR₃). The larger ligands ($\theta = 160^\circ$)¹⁶ failed to displace any COD (Table 1. 2).¹⁴

Table 1.2. Enthalpies for the Reaction of L (L = PR₃) with Ni(COD)₂ in Toluene

at 25° C

Ligand	θ^a (deg)	$-\Delta H(\text{kcal/mol})$	Product	D(Ni-P)
P(OEt) ₃	109	48	NiL ₄	36.8(1)
P(O- <i>i</i> -Pr) ₃	130	44	NiL ₄	36.2(1)
P(OPh) ₃	128	39	NiL ₄	34.5(1)
PMe ₃ , P(O- <i>p</i> -toly) ₃	118, 128	36	NiL ₄	33.7(1)
P(O- <i>o</i> -toly) ₃	141	20	(COD)NiL ₂	34.5(1)
PEt ₃ , PBut ₃	132	17	NiL ₃	38.6(1)
PPhEt ₂	136	15	NiL ₃	38.0(1)
P(O- <i>o</i> -C ₆ H ₄ - <i>i</i> -Pr) ₃	148	15	(COD)NiL ₂	32.0(1)
PPh ₃	145	8	NiL ₃	35.6(1)
P(O- <i>o</i> -C ₆ H ₄ - <i>t</i> -But) ₃	175	0	None	

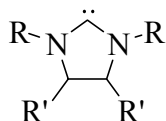
^a Data from Ref 16

1.3 *N*-Heterocyclic Carbenes as Ancillary Ligands

In the past few years *N*-heterocyclic carbene ligands (NHC) have gained increasing attention as a new class of ligands for homogenous catalysis.¹⁷ The NHC ligand class (Figure 1.1) ¹⁸ is often regarded as “*phosphine mimics*” because of their two electron donor ability. However, most of the NHCs have been found to possess stronger donor ability than even the

most basic phosphines. Therefore, they have been an attractive alternative to tertiary phosphines as ligands in homogenous organometallic chemistry.^{17b}

Figure 1.1. Nucleophilic *N*-Heterocyclic Carbenes



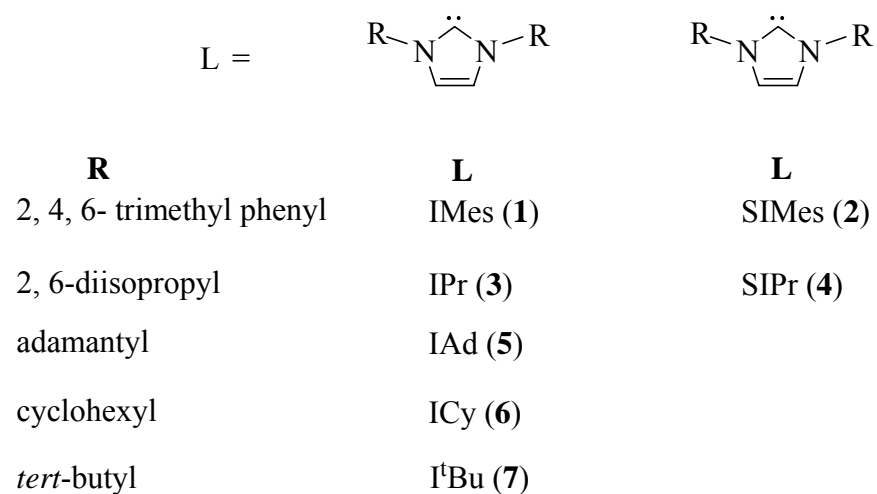
R = alkyl, aryl, ether,...

1.3.1 Structure and Fundamental Characteristics

Singlet *N*-heterocyclic ligands are neutral compounds with a divalent carbon atom having two non-bonding electrons. (Figure 1.1).¹⁸ The unusual stability of these NHCs has been a subject of many studies and various factors which include steric and kinetic effects have been explored.¹⁹ Electronegativity effects of the imidazole nitrogen, π -interactions in the imidazole ring and the large singlet-triplet gap in imidazole-2-ylidenes have also been studied.²⁰ These studies indicated that major contribution to NHC stabilization is the $p\pi$ - $p\pi$ electron donation from the nitrogen electron-pairs into the formally vacant p orbital of the carbenic carbon. This makes the carbenic carbon more nucleophilic.²¹

The basicity of these ligands is affected by the steric/electronic property of the R group at 1- and 3- positions of the imidazolium ring.²² For instance, presence of an electron donating alkyl group on nitrogens of the imidazole ring, makes the NHC more nucleophilic than NHC with an aryl group on imidazole nitrogens. Different NHCs have been synthesized and their activity studied.²³ The most popular NHCs are shown in Figure 1.2.

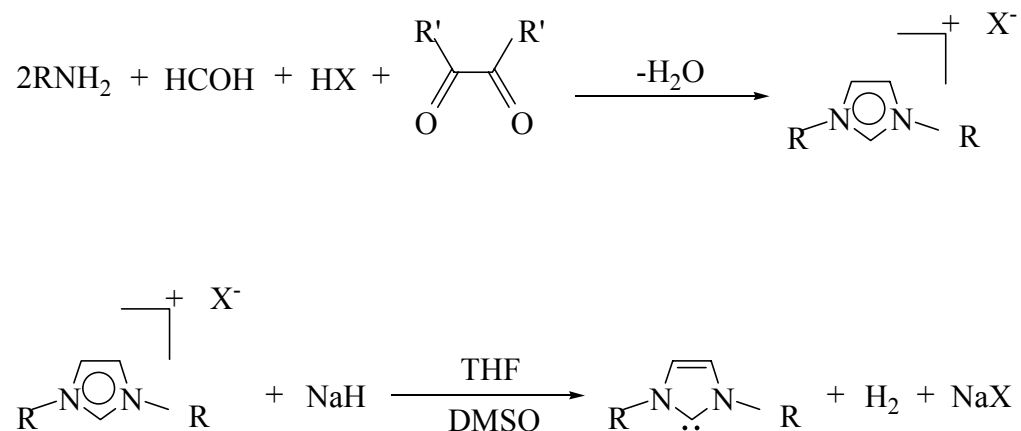
Figure 1.2. Common Saturated and Unsaturated *N*-Heterocyclic Carbenes



1.3.2. Synthesis of *N*-heterocyclic Carbenes

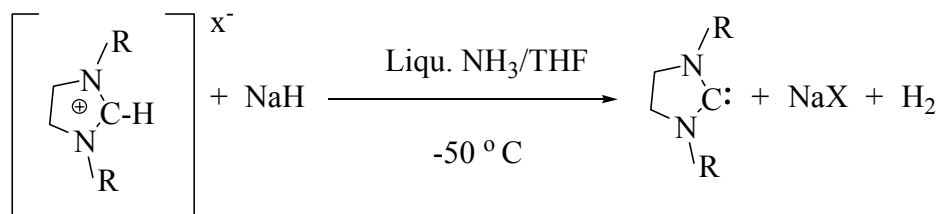
The first attempts to isolate free NHC were performed by Wanzlick in 1960.²⁴ However, the first isolated species was reported by Arduengo and co-workers in 1991 (Scheme 1.2).²⁵

Scheme 1.2. Synthesis of Imidazolium Salts and Generation of Free Carbene



Later on in 1996, Herrmann et al reported a general novel method, the liquid ammonia route, for the deprotonation of *N*-substituted azolium salts.²⁶ This route allowed the thermally labile free carbene to be generated for the first time (Scheme 1.4).

Scheme 1.3. Liquid Ammonia Route



R = CH₃, *c*-C₆H₁₁

1.4. Calorimetric Studies of Carbenes as Ancillary Ligands

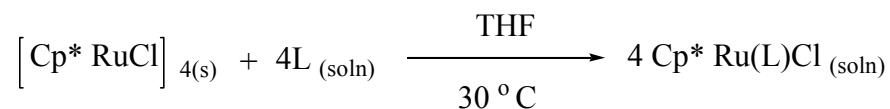
Recently thermochemistry studies have been applied to better understand the steric and electronic effects of NHCs.²⁷ This was first done by measuring the enthalpy value of the reaction of NHCs with an electron deficient ruthenium complexes stabilized as tetramer [cp*RuCl]₄ (SCHEME 1.4).^{27c} All carbene ligands investigated react rapidly and quantitatively with the [cp*RuCl]₄ tetramer. The reactions were all found to be exothermic. The enthalpy value (Scheme 1.4) is a measure of the binding properties of the ligands, the higher the value, the better nucleophilic the ligand is. In this study all NHC ligands were found to possess better electron donating properties with regard to binding the cp*RuCl moiety than the common phosphine ligands such as PCy₃ (-41 kcal/mol) and P(*i*-Pr)₃ (-37.4 kcal/mol), indicating increased electron donor properties of these ligands compared to the bulky electron-donating phosphines.^{27c}

Steric factors appear to play an important role in this series. Enthalpy of the reaction between IAd and [Cp*RuCl] is only -27.4 kcal/mol, even less than basic phosphines such as PCy₃ (-41.9 kcal/mol).

1.5 Metal-Carbene Complexes

Metal-carbene complexes were first discovered by Fischer and Mossböl in 1964 and has led to a huge number of applications in synthesis and catalysis since then.²⁸ The use of NHC-modified organometallic systems have been well recognized in palladium catalyzed Suzuki type reactions²⁹ as well as ruthenium metathesis.³⁰

Scheme 1.4. Enthalpies of Substitution (kcal/mol) for the Reaction



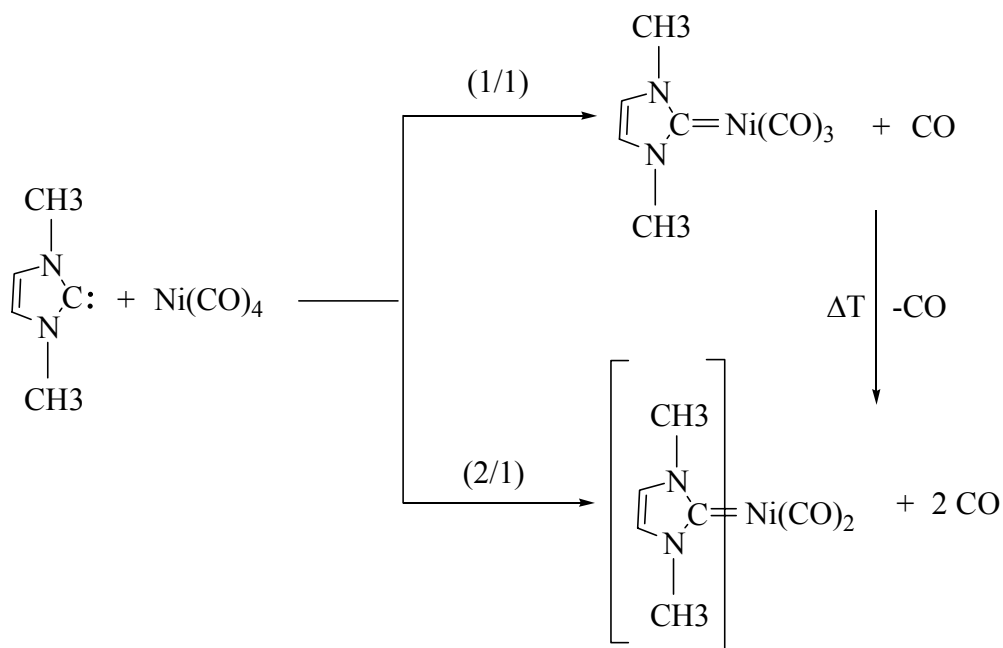
L	$-\Delta H_{\text{rxn}}$ (kcal/mol)
ICy	85
IAd	27.4
IMes	62.6
PCy ₃	41.9
P ⁱ Pr ₃	37.4

1.5.1 Nickel Complexes of *N*-Heterocyclic

The first Ni(0)-NHC complexes were prepared by Herrmann et al in 1993. They showed that free carbenes (L) derived from imidazole and triazole generated from azolium precursor salts react with Ni(CO)₄ to give the substitution products Ni(CO)₃L and Ni(CO)₂L₂ (Scheme 1.5).^{31c}

Since then various Ni(0)-NHC complexes have been prepared and characterized thoroughly.³¹

Scheme 1.5. Substitution Reactions of Ni(CO)₄ and (*N*, *N'*-bis(methylimidazol)-2-ylidene



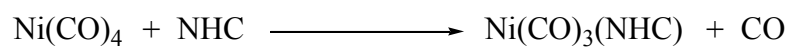
1.5.2 Ni-NHC Bond Energies

In 2003, Nolan et al carried out a series of substitution reactions of NHC ligands with Ni(CO)₄, which led to the formation of three and four coordinate Ni-NHC complexes.^{31e} It was observed that a relief of steric pressure around the metal center plays a major role in the formation of these types of complexes. Formation of four coordinate nickel compounds in the reaction of Ni(CO)₄ with NHC ligands such as IMes [*N,N'*-bis(2,4,6-trimethylphenyl)-imidazol]-

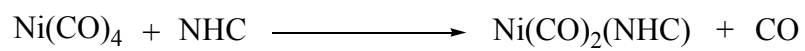
2-ylidene]), ICy [*N,N'*-bis(cyclohexylimidazol)-2-ylidene] at room temperature proved that these ligands were bulky enough to substitute only one carbonyl group to form stable four coordinate nickel complexes of the type $\text{Ni}(\text{CO})_3(\text{NHC})$ ($\text{NHC} = \text{ICy}, \text{IMes}$) (Scheme 1.6). However, substitution reaction of $\text{Ni}(\text{CO})_4$ with bulkier NHCs such as I^tBu [*N,N'*-bis(*tert*-butylimidazol)-2-ylidene] and IAd [*N,N'*-bis(1-adamentylimidazol)-2-ylidene]) resulted in the formation of three coordinate nickel complexes, in which two carbonyl groups were forced to dissociate from the metal center in order to accommodate one sterically demanding I^tBu and IAd ligands. (Scheme 1.6).

To measure the Ni-NHC bond energies both complexes $\text{Ni}(\text{CO})_2\text{IAd}$ and $\text{Ni}(\text{CO})_2(\text{I}^t\text{Bu})$ were reacted with CO in a high pressure FTIR cell.³² It was observed that both complexes react with CO to produce $\text{Ni}(\text{CO})_4$. However, no equilibrium was observed between saturated three coordinate nickel complexes and $\text{Ni}(\text{CO})_4$. The equilibrium established between three coordinate $\text{Ni}(\text{CO})_2(\text{NHC})$ ($\text{NHC} = \text{I}^t\text{Bu}, \text{IAd}$) was used to afford thermodynamic parameters and led to the measurement of Ni-NHC ($\text{NHC} = \text{I}^t\text{Bu}, \text{IAd}$) bond energies. Ni-IAd bond (43 ± 3 kcal/mol) was found to be stronger than Ni- I^tBu bond (39 ± 3 kcal/mol) which shows the stronger donor ability of IAD compared to I^tBu .

Scheme 1.6. Substitution Reactions of Ni(CO)₄ and NHCs



NHC = ICy, IMes



NHC = IAd, I^tBu

1.6 References and Notes

1. Irvine, J. W. Jr.; Wilkinson, G. *Science*, **1951**, *13*, 742-743.
2. Wilkinson, G.; *J. Am. Chem. Soc.* **1951**, *73*, 5501-5502.
3. (a) Ugo, R. *Coor. Chem. Rev.* **1968**, *3*, 319-344. (b) Gosser, W.; Tolman, C. A. *Inorg. Chem.* **1970**, *9*, 2350-2357. (c) Schumann, H.; Stelzer, O.; Niederreuther, U.; Roesch, L.. *Chem. Ber.* **1970**, *103*, 1383-1390. (d) Tamao, K.; Sumith, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374-4375. (e) Schmidh, F. K.; Mironova, L. V.; Saraev, V. V.; Tkach, V. S.; Kalabiana, A. V. *React. Kinet. Catal. Lett.* **1976**, *4*, 73-79. (f) Mason, M. G.; Swepston, P. N.; Ibers, J. A. *Inorg. Chem.* **1983**, *22*, 411-418. (g) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *Inorg. Chem.* **1983**, *22*, 104-108. (h) Osakada, K.; Maeda, M.; Nakamura, Y.; Yamamoto, T.; Yamamoto, A. *J. Chem. Soc. Chem. Comm.* **1986**, *6*, 442-443.
4. Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956-2965.
5. Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953-2956.
6. Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Am. Chem. Soc.* **1959**, 2323-2327.
7. Meriwether, L. S.; Fiene, M. L. F. *J. Am. Chem. Soc.* **1959**, *11*, 181-183.
8. Chatt, J.; Hart, F. A. *J. Am. Chem. Soc. Abstracts*, **1960**, 1378-1389.
9. Bigorgne, M. *J. Inorg. Nucl. Chem.* **1964**, *26*, 197-115.
10. Horrocks, W. D. Jr.; Taylor, R. C. *Inorg. Chem.* **1963**, *2*, 723-727.
11. Strohmeier, W.; Müller, F. *J. Chem. Ber.* **1967**, *100*, 2812-2821.
12. Lalage, D.; Brown, S.; Connor, J. A.; Skinner, H. A. *J. Chem. Soc., Faraday I*, **1974**, *9*, 1649-1652.
13. Kiser, R. W.; Krasso, M. A.; Clark, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 3653-3654.

14. Tolman, C. A.; Rueter, D. W.; Seidel, W. C. *J. Org. Chem.* **1976**, *117*, C30-C33.
15. Handbook of chemistry and physics, 41st ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p. 1889.
16. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313-324.
17. (a) Wanzlik, H. –W. *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 75-80. For reviews see:
 (b) Hermann, W. A.; Köcher, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2163-2187. (c) Regitz, M. *Angew. Chem. Int. Ed. Engl.* 1996, *35*, 725-728. (d) Arduengo, A. J. III; Krafczyk, R. *Chem. Z.* **1998**, *32*, 6-14. (e) Bourissou, D.; Guerret, O.; Gabbai, F. D.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39-92. (f) Weskamp, T.; Böcher, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12-22. (g) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181-222.
18. Arduengo, A. J. III; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530-5534.
19. (a) Dixon, D. A.; Arduengo, A. J. III. *J. Phys. Chem.* **1991**, *95*, 4180-4182. (b) Arduengo, A. J. III; Block, H.; Chen, H.; Dixon, D. A.; Green, J. C.; Herrmann, W. A.; Jones, N. L.; Wagner, M.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 6641-6649. (c) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039-2946.
20. (a) Reference 11a (b) Reference 19b (c) Reference 19c (d) Arduengo, A. J. III; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetsle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812-6822. (e) Arduengo, A. J. III; Dixon, D. A.; Kumashiro, K. K.; Lee, C.; Power, W. P.; Zlim, K. W. *J. Am. Chem. Soc.* **1994**, *116*, 6361-6367. (f) Heinemann, C.; Thiel, W. *Chem. Phys. Lett.* **1994**, *217*, 11-

13. (g) Heinemann, C.; Müller, T.; Apeiloig, Y.; Schwartz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023-2038. (h) Sausers, R. R. *Tetrahedron lett.* **1996**, *37*, 149-152.
21. Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C. A.; Artus, G. R. J. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371-2374.
22. Huang, J.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370-2375.
23. (a) Reference 17c (b) Reference 17e (d) Herrmann, W. A.; Köcher, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162-2188.
24. (a) Wanzlick, H. -W.; Schikoro, E. *Angew. Chem. Int. ed. Engl.* **1960**, *72*, 494-498. (b) Wanzlick, H. -W.; Schikoro, E. *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 129-134. (c) Wanzlick, H. -W.; Schonher, H. -J. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141-142. (d) Wanzlick, H. -W.; Schonher, H. -J. *Liebigs, Ann. Chem.* **1970**, *731*, 176-179.
25. Arduengo, A. J. III.; Harlow, R. L.; Kline, M. J. *Am. Chem. Soc.* **1991**, *113*, 361-363.
26. Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Chem. Eur. J.* **1996**, *2*, 772-780.
27. (a) Smith, D. C. Jr.; Haar, C. M.; Stevens, E. D.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G. *Organometallics* **2000**, 1427-1433. (b) Freeman, S. T. N.; Lemke, F. R.; Haar, C. M.; Nolan, S. P.; Petersen, J. L. *Organometallics* **2000**, *19*, 4828-4833. (c) Laporte, C.; Frison, G.; Grutzmancher, H.; Hillie, A. C.; Sommer, W.; Nolan, S.P. *Organometallics* **2003**, *22*, 2202-2208. (d) Huang, J.; Schanz, H. H.; Stevens, E. D.; Nolan, S. P. *Inorg. Chem.* **2000**, *39*, 1042-1045. (e) Smith, D. C.

- Jr.; Haar, C. M.; Luo, L. C.; Cucullu, M. E.; Mahler, C. H.; Noal, S. P.; Marshall, W. J.; Jones, N. L.; Fagan, P. *Organometallics* **1999**, *18*, 2357-2361. (f) Huang, J.; Schanz, H.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370-2375.
28. (a) Herrmann, W. A.; Corniks, B. E. Applied Homogeneous Catalysis with Organotransition Compounds; VCH: Weinheim, Germany, 1996; Vol. 1; Vol 2. (b) Herrmann, W. A.; Reisinger, C. P.; Spiegle, M. J. *Organomet. Chem.* **1998**, *557*, 93-96. (c) Enders, D.; Gielen, H.; Raabe, G.; Runsinke, J.; Teles, J. H. *Chem. Ber.* **1996**, *124*, 1483-1488. (d) Navarro, O.; Kaur, H.; Mahjoor, P.; Nolan, S. P. *J. Org. Chem.* **2004**, *69*, 3173-3180. (e) Navarro, O.; Kaur, H.; Kelly, R. A., III; Nolan, S. P. *Organometallics* **2001**, *20*, 2878-2882. (f) Jafarpour, L.; Noal, S. P. *J. Organomet. Chem.* **2001**, *17*, 617-618. (g) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 2416-2419.
29. (a) Huang, J.; Stevens, E. D.; Noal, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 2674-2678. (b) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *617*, 17-27. (c) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18-29.
30. (a) Arduengo, A. J. III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. J. *Am. Chem. Soc.* **1994**, *116*, 4391-4394. (b) Herrmann, W. A.; Goosen, L. J.; Artus, G. R. J.; Köcher, C. *Organometallics* **1997**, *16*, 2472-2477. (c) mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 9976-9977. (d) Hou, H.; Gantzel, P. K.; Kubiak, G. P. *Organometallics* **2003**, *22*, 2817-2819. (e) Dorta, R. ;

Stevens, E. D. ; Hoff, C. D. ; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490-10491.

31. For the experimental design of FTIR cell see : (a) Bender, B. R.; Kubas, G. J.; Jones, L. H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179-9190.

CHAPTER 2

Synthetic, Structural and Thermochemical Studies of *N*-Heterocyclic Carbene (NHC) and Tertiary Phosphine Ligands in the $\text{Ni}(\text{CO})_2(\text{L})_2$ ($\text{L} = \text{PR}_3$, NHC) Systems

2.1. Introduction

Since the first report of the synthesis of isolable *N*-heterocyclic carbenes (NHC) by Arduengo and co-workers,¹ increasing attention has been focused on employing NHC as ancillary ligands in organometallic chemistry and homogeneous catalysis.² The NHC ligand class (Figure 2.1) are often regarded as "*phosphine mimics*",³ because of their two electron donor ability. However, most of the NHCs have been found to possess stronger electron donating properties than even the most basic phosphine, making them an attractive alternative to this ubiquitous ligand family.^{2b} Although some of the beneficial use of NHC-modified organometallic systems have been widely studied in palladium catalyzed Suzuki type reactions⁴ as well as ruthenium olefin metathesis,^{5,2i} nickel NHC complexes have been less explored.⁶ In situ generated $\text{Ni}(0)$ -*N*-heterocyclic complexes have been found to possess high activity in various catalytic systems.⁷⁻⁹ However, less attention has been focused on the preparation and use of well-defined $\text{Ni}(0)$ -NHC catalysts.¹⁰

Recent thermochemical studies in our group have indicated that 1,3-disubstituted imidazol-2-ylidene carbene ligands have better electron donating properties than phosphine ligands.¹¹ The basicity of these ligands is affected by the steric/electronic property of the R group at the 1- and 3- positions of the imidazolium ring.^{3d} We were able to apply this primary principle in modifying C-C cross coupling reactions¹² and catalytic ruthenium based olefin metathesis.^{5a} We now wish to report the synthesis, structural characterization and thermochemistry of complexes of type $\text{Ni}(\text{CO})_2(\text{L})_2$ ($\text{L} = \text{PR}_3, \text{NHC}$) which enables the determination of Ni-NHC ($\text{NHC} = \text{ICy}, \text{IMes}$) and Ni-P ($\text{P} = \text{PCy}_3, \text{PPh}_3, \text{P}(p\text{-Tol})_3, \text{P}(m\text{-Tol})_3$) bond dissociation energies.

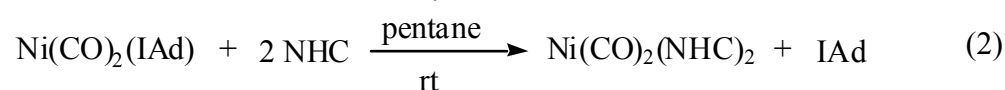
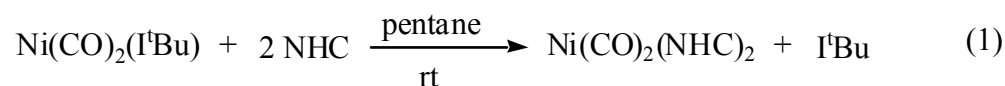
2.2 Results and Discussion

2.2.1 Synthesis and Structure Determination of $\text{Ni}(\text{CO})_2(\text{ICy})_2$ (8) and $\text{Ni}(\text{CO})_2(\text{IMes})_2$ (9).

We have recently reported the synthesis of stable three and four coordinate nickel-NHC complexes in which steric and electronic effect of NHC ligands were investigated in the series of substitution reactions with $\text{Ni}(\text{CO})_4$.¹³ It was observed that a relief of steric pressure around the metal center plays a major role in the formation of these types of complexes. Formation of four coordinate nickel compounds in the reaction of $\text{Ni}(\text{CO})_4$ with NHC ligands such as IMes (**1**), ICy (**6**) and IPr (**3**) at room temperature proved that these ligands were bulky enough to substitute only one carbonyl group to form stable nickel complexes of the type $\text{Ni}(\text{CO})_3(\text{NHC})$. However substitution reactions of $\text{Ni}(\text{CO})_4$ with I^tBu and IAd resulted in the formation of three coordinate nickel complexes in which two carbonyl groups were forced to dissociate from the metal center in order to accommodate one sterically demanding I^tBu or IAd ligands. In the present work we were able to prepare Ni di-carbonyl complexes using less bulky NHC ligands. This was carried

out using the substitution reactions of $\text{Ni}(\text{CO})_2(\text{NHC})$ ($\text{NHC} = \text{I}^t\text{Bu}$, IAd) with ICy and IMes in which sterically hindered I^tBu and IAd were replaced with two smaller NHCs (IMes and ICy) at room temperature according to eq 1 and 2 (Scheme 2.1). Both reactions proceed in high yields.

Scheme 2.1. Synthesis of Complexes $\text{Ni}(\text{CO})_2(\text{ICy})_2$ (**8**) and $\text{Ni}(\text{CO})_2(\text{IMes})_2$ (**9**)



($\text{NHC} = \text{ICy}, \text{IMes}$)

^1H and ^{13}C NMR spectra as well as elemental analysis support the structure of the products as $\text{Ni}(\text{CO})_2(\text{ICy})_2$ (**8**) and $\text{Ni}(\text{CO})_2(\text{IMes})_2$ (**9**) respectively. Infrared data indicated that ICy ($A_1\nu_{\text{co}}$ for $\text{Ni}(\text{CO})_2(\text{ICy})_2 = 1948.5 \text{ cm}^{-1}$) is a better donor than IMes ($A_1\nu_{\text{co}}$ for $\text{Ni}(\text{CO})_2(\text{IMes})_2 = 2050.5 \text{ cm}^{-1}$).

Figure 2.1. Ball and Stick Structure of $\text{Ni}(\text{CO})_2(\text{ICy})_2$ (8)

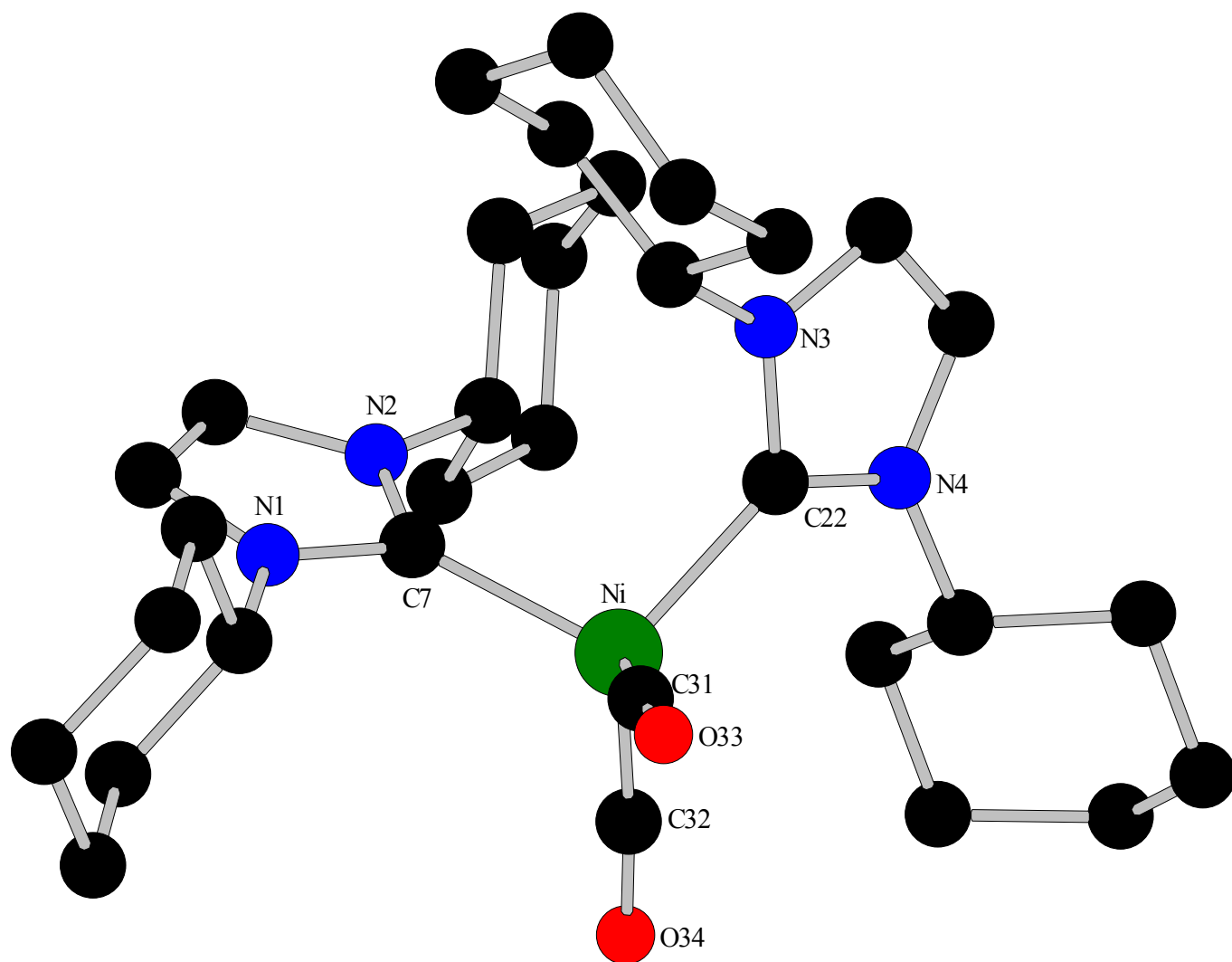
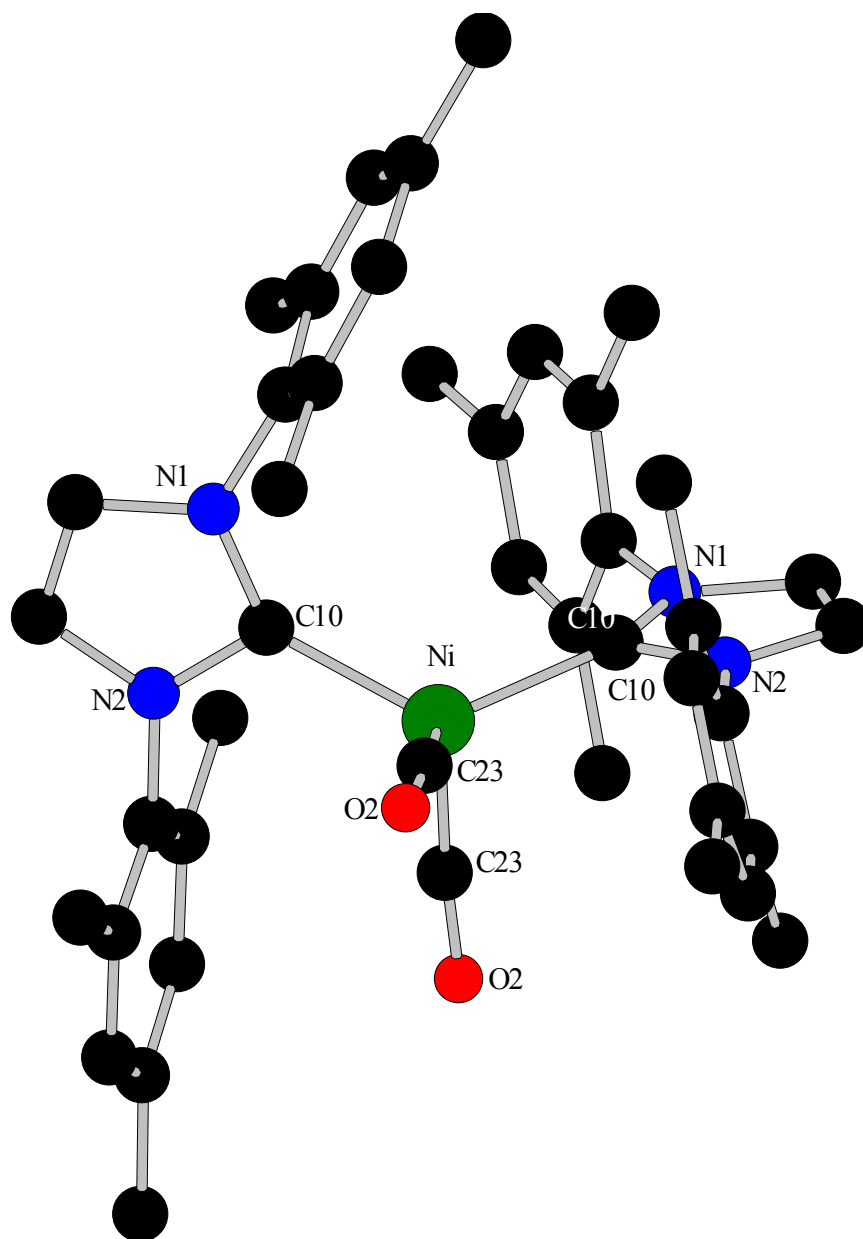


Figure 2.2. Ball and Stick Structure of $\text{Ni}(\text{CO})_2(\text{IMes})_2$ (**9**)



Crystals suitable for X-ray analysis were grown from pentane at -50°C . X-ray structures of $\text{Ni}(\text{CO})_2(\text{ICy})_2$ (**8**) and $\text{Ni}(\text{CO})_2(\text{IMes})_2$ (**9**) are depicted in Figures 2.2 and 2.3 respectively. Crystallographic data are listed in Table 2.1 and selected bond lengths and angles are given in Table 2.2. The geometry about nickel is tetrahedral as expected for an 18 electron $\text{Ni}(0)$

complexes.¹⁴ The NHCs exhibit a *cis* configuration around the metal center. Carbonyl groups are *cis* to each other. The Ni-C_{carbenic} average bond length of 2.002(4) Å for compound **8** and 1.983(3) Å for compound **9** are comparable to that in other Ni(0) carbene complexes that have been structurally characterized.^{13, 16, 18} The structure of **8** and **9**, in combination with previously reported structures of four coordinate Ni(0) complexes,^{13, 16, 18} complete the crystallographic characterization of this class of complexes. A comparison of the structural data for four coordinate Ni(0)-*N*-heterocyclic complexes show that these complexes were surprisingly similar. The electron density at the metal center increases with increased donating ability of the NHC ligand. Thus, the enhanced metal-carbonyl back-bonding leads in the same order to shortening of the metal-carbon bond and to a lengthening of the carbon-oxygen bond in the carbonyl ligands. However, essentially no significant change was observed in Ni-C bond and C-O bond distances in the range of *N*-heterocyclic ligands of different bulk and different electron donating property (the longest Ni-C bond distance was found for Ni(CO)₃L¹⁶ (L = [N,N'-bis(1'-phenylethylimidazoline)-2-ylidene]), 1.794(4) Å and the shortest Ni-C bond was found for Ni(CO)₂(L)₂(L = [N,N'-bis(methylimidazol)-2-ylidene]), 1.758(5) Å,¹⁸ Ni(CO)₂(ICy)₂ (**8**) was found to have the longest C-O bond distance of 1.165(5) Å, and Ni(CO)₃(L)¹⁶ (L = [N,N'-bis(1'-phenylethylimidazoline)-2-ylidene]) show the shortest C-O bond distance of 1.134(5) Å) (Table 2.3).

Table 2.1. Crystallographic Data for Compounds Ni(CO)₂(NHC)₂

	8	9
empirical formula	C ₃₂ H ₄₈ N ₄ NiO ₂	C ₄₄ H ₄₈ N ₄ NiO ₂
fw	579.45	723.57
space group	P2 ₁ /C	Pccn
cryst syst	monoclinic	orthorhombic
a, Å	11.1412(18)	10.7392(6)
b, Å	18.133(3)	18.4417(10)
c, Å	16.174(3)	20.2836(11)
a, deg	90	90
b, deg	103.358	90
g, deg	90	90
μ (Mo), mm ⁻¹	0.643	0.523
Z	4	4
R	0.0355	0.0316
R _w	0.0739	0.0607
no. of refined params	542	323
no. of data collected	10319	38689
no. of unique data, I>2σ	4019	1876
R _{merge}	0.0709	0.0471

Table 2.2. Selected Bond Lengths (Å) and Bond Angles (deg)
for Ni(CO)₂(NHC)₂ Complexes

Compound 8			
Ni-C(7)	2.023(4)	C(31)-O(33)	1.158(5)
Ni-C(22)	1.991(4)	C(32)-C(34)	1.170(5)
Ni-C(31)	1.789(5)	N(1)-C(1)	1.480(5)
Ni-C(32)	1.762(5)	N(2)-C(10)	1.489(5)
C(32)-Ni-C(31)	113.6(2)		
C(22)-Ni-C(7)	100.95(16)		
Compound 9			
Ni-C(10)	1.983(3)	N(1)-C(1)	1.440(4)
Ni-C(23)	1.761(3)	N(2)-C(13)	1.438(4)
Ni-C(23)-O	1.161(3)		
C(23)-Ni-C(23)	105.61(18)		
C(10)-Ni-C(10)	124.22(17)		

Direct comparison of enthalpies of reaction for ICy (-29.0 ± 3.0 kcal/mol) and IMes (-14.8 ± 3.0 kcal/mol) gives a difference of 6 kcal/mol. The strong donor property of the NHC ligands, draw the electron density on the metal center and increases the metal-carbonyl back-bonding. As a result of this higher electron density on the nickel center, we expected NHC ligands of stronger donor ability to have a shorter Ni-C_{carbene} bond length and longer C-O bond distance, but no significant bond alternation was observed. The longest Ni-C_{carbenic} distance was observed for Ni(CO)₂(ICy)₂ (**8**) (2.002(4) Å) while the shortest distance was found for Ni(CO)₃(SIMes) (1.961(3) Å) (Table 2.3).

Table 2.3. Selected Bond Lengths (Å) in Carbonylnickel-Carbene Complexes

	Ni-C	C-O	Ni-C _{carbene}
Ni(CO) ₄ ^a	1.817(3)	1.127(3)	
Ni(CO) ₂ (ICy) ₂ (8)	1.775(5)	1.164(5)	2.002(4)
Ni(CO) ₃ L ^b	1.794(4)	1.134(5)	1.986(3)
Ni(CO) ₂ (IMes) ₂ (9)	1.791(3)	1.161(3)	1.983(3)
Ni(CO) ₂ L ₂ ^c	1.758(5)	1.147(5)	1.977(4)
Ni(CO) ₃ (IPr) ^d	1.790(3)	1.145(3)	1.972(2)
Ni(CO) ₃ (IMes) ^d	1.793(4)	1.144(4)	1.971(3)
Ni(CO) ₃ (SIPr) ^d	1.789(4)	1.143(4)	1.962(4)
Ni(CO) ₃ (SIMes) ^d	1.780(3)	1.148(3)	1.961(3)

^a Data from ref 15. ^b Data from ref 16 (L = [N,N'-bis(1'-phenylethylimidazoline)-2-ylidene]).^c

Data from ref 18 (L = [N,N'-bis(methylimidazol)-2-ylidene]) . ^d Data from ref 13.

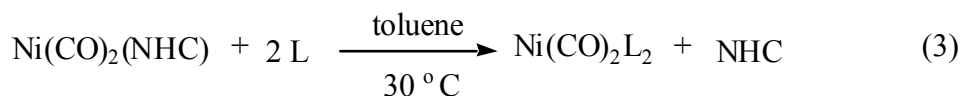
The electron density at the metal center increases with the number of NHC ligands systematically, therefore Ni(CO)₃(IMes) is expected to have a longer Ni-C_{carbene} bond compare to Ni(CO)₂(IMes)₂ (**9**), however the stronger steric effect of two carbene ligands on the metal center overcomes the better donating property of two IMes ligand on the nickel center, making Ni-C_{carbene} longer for Ni(CO)₂(IMes)₂ (**9**) as compared to Ni(CO)₃(IMes) (Table 2.3).

2.2.2 Calorimetric Studies

We have recently reported the synthesis and characterization of three and four coordinate nickel carbonyl complexes of the type Ni(CO)₂(NHC) (NHC = I^tBu (**7**), IAd (**5**)) and Ni(CO)₃(NHC) (NHC = ICy (**6**), IMes (**1**)) and it was reasoned that the equilibrium associated with Ni(CO)₄ and NHC could be a key to the measurement of Ni-NHC bond energies.¹³ We were

successfully able to evaluate the bond dissociation energy of Ni and sterically hindered I^tBu and IAd (BDE for Ni-I^tBu = 39 ± 3.0 kcal/mol, BDE for Ni-IAd = 43 ± 3.0 kcal/mol) based on the equilibrium established between three coordinate Ni(CO)₂(NHC) (NHC = I^tBu, IAd) and Ni(CO)₄. However, no equilibrium was established between saturated Ni(CO)₃(NHC) (NHC = ICy, IMes) and Ni(CO)₄. In the present work in order to evaluate bond dissociation energy of Ni-L (L = NHC (ICy, IMes), tertiary phosphine (PCy₃, PPh₃, P(*p*-Tol)₃, P(*m*-Tol)₃) and to better understand the fundamental steric and electronic factors governing NHC ligands and to afford a direct comparison with a large array of tertiary phosphine data,¹⁷ we have carried out the substitution reactions depicted in eq 3 (scheme 2.2). These reactions are suitable for calorimetric studies since they were all found to be rapid and quantitative by NMR.

Scheme 2.2. Substitution Reactions of Ni(CO)₂(NHC)



NHC = I^tBu, IAd

L = NHC (ICy, IMes)

PR₃ (PPh₃, PCy₃, P(*p*-Tol)₃, P(*m*-Tol)₃)

The enthalpy values were determined by anaerobic solution calorimetry in toluene at 30 °C by reacting 2 equivalent of the NHC or phosphine ligands with 1equivalent of Ni(CO)₂(NHC) [NHC = I^tBu (**7**), IAd (**5**)] and the data are shown in Table 4 and 5 respectively. The magnitude of the enthalpy of reaction is affected by both steric and electronic nature of the ligands. Both carbene ligands ICy (**6**) (entry 1) and IMes (**1**) (entry 2) show more exothermic reaction enthalpy

than even the most basic phosphine PCy₃ (entry 3), indicating the greater donor property of these ligands.

Table 2.4. Enthalpies of Substitution (kcal/mol) in the Reaction

$$[\text{Ni}(\text{CO})_2(\text{ItBu})]_{(\text{soln})} + 2 \text{L}_{(\text{soln})} \xrightarrow[30\text{ }^\circ\text{C}]{\text{toluene}} \text{Ni}(\text{CO})_2(\text{L})_2_{(\text{soln})}$$

entry	L	$-\Delta H_{\text{rxn}}(\text{kcal/mol})^{\text{a}}$
1	ICy	20.9(0.2)
2	IMes	14.8(0.6)
3	PCy ₃	12.6(0.1)
4	tri- <i>p</i> -tolylphosphine	11.8(0.3)
5	tri- <i>m</i> -tolylphosphine	11.5(0.3)
6	PPh ₃	10.7(0.2)

^a Heat of Solution is included. ^b Enthalpy values are reported with 95% confidence limits.

Table 2.5. Enthalpies of Substitution (kcal/mol) in the Reaction

$$[\text{Ni}(\text{CO})_2(\text{IAd})]_{(\text{soln})} + 2 \text{L}_{(\text{soln})} \xrightarrow[30\text{ }^\circ\text{C}]{\text{toluene}} \text{Ni}(\text{CO})_2(\text{L})_2_{(\text{soln})}$$

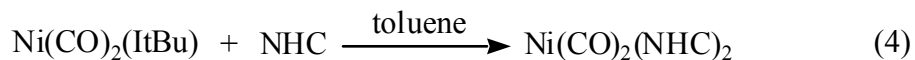
entry	L	$-\Delta H_{\text{rxn}}(\text{kcal/mol})^{\text{a}}$
1	ICy	17.5(0.3)
2	IMes	13.4(0.2)
3	PCy ₃	12.0(0.2)
4	tri- <i>p</i> -tolylphosphine	11.9(0.3)
5	tri- <i>m</i> -tolylphosphine	11.0(0.3)
6	PPh ₃	10.2(0.2)

^a Heat of Solution is included. ^b Enthalpy values are reported with 95% confidence limits.

No reaction was observed between *ortho* substituted phosphine ligands (tri-*o*-tolylphosphine and tri-*o*-methoxyphenylphosphine) and Ni(CO)₂(NHC) (NHC = I^tBu, IAd), showing the importance of steric effects in these reactions. The greater cone angle of tri-*o*-tolylphosphine ($\theta = 194 \pm 6^\circ$)¹⁷ and tri-*o*-methoxyphenylphosphine ($\theta = 165^\circ \pm 10$)²² affects the availability of electron pair on phosphorus to coordinate to the nickel center and therefore there is no reaction. However, the reaction takes place with P(*p*-Tol)₃ ($\theta = 143^\circ$)¹⁷ (entry 4) and P(*m*-Tol)₃ ($\theta = 165^\circ$)²² (entry 5) which has smaller cone angle and therefore is less sterically hindered. The enthalpy values for the reaction of Ni(CO)₂(IAd) (Table 2.5) show a similar pattern as for that found for Ni(CO)₂(ItBu). However, the magnitude of enthalpy of the reaction is marginally smaller. The Ni-IAd bond (43 ± 3.0 kcal/mol) is a stronger bond than Ni-I^tBu (39 ± 3.0 kcal/mol), therefore breaking this bond with nucleophilic ligands requires more energy, so that the overall enthalpy of the reaction is less exothermic than reactions which involve breaking Ni-I^tBu bond.

2.2.3 Absolute Ni-NHC and Ni-P Bond Enthalpies.

The enthalpies of the substitution reactions of the type shown in eq 3 can be used to evaluate the Ni-NHC bond dissociation energies as well as Ni-P bond dissociation energies. Using the enthalpies of solution for the substitution reaction of Ni(CO)₂(I^tBu) with ICy (-20.9 ± 0.2 kcal/mol) or IMes (-14.8 ± 0.6 kcal/mol) and previously published bond dissociation energy of Ni-I^tBu (39.0 ± 3.0 kcal/mol),¹³ these data were used to calculate bond dissociation energy of Ni-ICy (BDE for Ni-ICy, 29.9 ± 3.0 kcal/mol) and Ni-IMes (BDE for Ni-IMes, 26.9 ± 3.0 kcal/mol) according to eq 4 (Scheme 2.3).

Scheme 2.3. Substitution Reaction of Ni(CO)₂(I^tBu)

$$\Delta H_{\text{rxn}} = \{ - 2 \text{ BDE (Ni-NHC)} + \text{BDE (Ni-I}^t\text{Bu)} \}$$

(NHC = ICy, IMes)

Substitution reactions involving Ni(CO)₂(IAd) and ICy or IMes give the bond dissociation value of 30.2 ± 3.0 kcal/mol for Ni-ICy and 28.2 ± 3.0 kcal/mol for Ni-IMes. There is a reasonable agreement between two values obtained for Ni-ICy and Ni-IMes BDE from Ni(CO)₂(I^tBu) and Ni(CO)₂(IAd) substitution reactions, which yield an average of 30.0 ± 3.0 kcal/mol for Ni-ICy and 27.5 ± 3.0 kcal/mol for Ni-IMes bond dissociation energies. The bond strength for nickel-phosphine can be calculated in a same manner. The average bond dissociation energies are shown in Table 2.6.

Table 2.6. Bond Dissociation Energies of Ni-NHC and Ni-P

entry	L	BDE
1	ICy	30.0(3.0)
2	IMes	27.5(3.0)
3	PCy ₃	26.6(3.0)
4	tri- <i>p</i> -tolylphosphine	26.4(3.0)
5	tri- <i>m</i> -tolylphosphine	26.1(3.0)
6	PPh ₃	25.7(3.0)

Both NHC ligands ICy and IMes possess stronger bond dissociation energies, showing that NHC ligands are among the strongest ligands known for Ni(0).^{19, 20} The relative BDE values for Ni-ICy (30.0 ± 3.0 kcal/mol) and Ni-IMes (27.5 ± 3.0 kcal/mol) are in accord with the infrared data which indicate that ICy (ν_{co} for $\text{Ni}(\text{CO})_2(\text{ICy})_2 = 1948.6 \text{ cm}^{-1}$) is a better donor than IMes (ν_{co} for $\text{Ni}(\text{CO})_2(\text{IMes})_2 = 2050.5 \text{ cm}^{-1}$). The strongest nickel-phosphine bond dissociation energy was found for the most basic phosphine, PCy₃ (BDE for Ni-PCy₃, 26.6 ± 3.0 kcal/mol) and Ni-PPh₃ was found to give the weakest bond strength (BDE for Ni-PPh₃, 25.7 ± 3.0 kcal/mol).

A calorimetric study of the reactions of various phosphorus ligands (and t-BuNC) with Ni(COD)₂ (COD = 1,5-cyclooctadienenickel) by Tolman²⁰ showed that both the extent of reaction and mean Ni-P bond strengths tend to decrease with increasing ligand size; P(OMe)₃ ($\theta = 107^\circ$)¹⁷ was found to give the highest enthalpy value of -57 kcal/mol in the formation of NiL₄ (L = P(OMe)₃). While the reaction of bulky P(O-*o*-C₆H₄-i-Pr)₃ ($\theta = 148^\circ$)¹⁷ and Ni(COD)₂ resulted in the formation of Ni(COD)(L)₂ (L = P(O-*o*-C₆H₄-i-Pr)₃) and found to give the lowest enthalpy value of -15 kcal/mol. However, enthalpy values (Table 2.3) in our system show that BDE of Ni-P in the formation of Ni(CO)₂(PR₃)₂ complexes is dependent on the electron donor-acceptor character of the phosphorus ligand. The decreasing exothermicity in the formation of Ni(CO)₂(PR₃)₂ [PR₃ = PCy₃, PPh₃, P(*p*-Tol)₃, P(*m*-Tol)₃] which results in a smaller BDE values (Table 2.6) corresponds closely to the decreasing electron donating ability of the phosphorus ligand. The most basic phosphine, PCy₃ (entry 3), which has the greatest cone angle ($\theta = 170^\circ$)¹⁶ shows the strongest bond dissociation energy which indicates the dominant effect of electronic in the magnitude of Ni-P bond dissociation energy.

2.3 Conclusions

The synthesis and structural characterization of $\text{Ni}(\text{CO})_2(\text{ICy})_2$ (**8**) and $\text{Ni}(\text{CO})_2(\text{IMes})_2$ (**9**) is described. No significant bond alternation was found in the $\text{Ni-C}_{\text{carbene}}$ bond lengths. All ligands investigated react rapidly and quantitatively in the substitution reaction of $\text{Ni}(\text{CO})_2(\text{I}^t\text{Bu})$ and $\text{Ni}(\text{CO})_2(\text{IAd})$. NHC ligands ICy and IMes show better electron donating properties than tertiary phosphine ligands. Steric factors appear to play an important role in the formation of $\text{Ni}(\text{CO})_2(\text{L})_2$ ($\text{L} = \text{ICy}, \text{IMes}, \text{PCy}_3, \text{PPh}_3, \text{P}(p\text{-Tol})_3, \text{P}(m\text{-Tol})_3$). The enthalpy values of the formation of $\text{Ni}(\text{CO})_2(\text{L})_2$ ($\text{L} = \text{ICy}, \text{IMes}, \text{PCy}_3, \text{PPh}_3, \text{P}(o\text{-Tol})_3, \text{P}(m\text{-Tol})_3$) have been measured by solution calorimetry and used to evaluate Ni-NHC and Ni-P bond dissociation energies.

2.4 Experimental Section

General Considerations. All reactions were performed under an inert atmosphere of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in an MBraun glovebox containing less than 1 ppm oxygen and water. Solvents were distilled from appropriate drying agents or were passed through an alumina column in an MBraun solvent purification system, other anhydrous solvents were purchased from Aldrich and degassed prior to use by purging with dry argon and were kept over molecular sieves. Solvents for NMR spectroscopy were degassed with argon and dried over molecular sieves. NMR spectra were recorded on a 400 MHz Varian Gemini. Infrared spectra were recorded on a PE 2000 FT-IR spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80), which was periodically calibrated using the TRIS¹⁸ reaction or the enthalpy of solution of KCl in water.¹⁹ Experimental enthalpy data are reported with 95% confidence limit. Elemental analysis was

performed at Desert Analysis, Tucson, AZ. PPh_3 , PCy_3 , tri-*p*-tolylphosphine, tri-*m*-tolylphosphine, tri-*o*-tolylphosphine, tri-*o*-methoxyphenylphosphine, were used as received (Strem). The identity of nickel phosphine complexes: $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$,²⁶ $\text{Ni}(\text{CO})_2(\text{PCy}_3)_2$,²⁶ $\text{Ni}(\text{CO})_2(\text{tri-}p\text{-tolylphosphine})_2$,²⁷ $\text{Ni}(\text{CO})_2(\text{tri-}m\text{-tolylphosphine})_2$,²⁷ were confirmed by comparison with literature spectroscopic data

NMR Titrations. Prior to every set of calorimetric experiments, a Wilman screw-capped NMR tube was charged with (± 0.1 mg) of organometallic complex and fitted with a septum, and toluene- d_8 was subsequently added. A solution of the ligand of interest was then injected to the NMR tube through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ^1H NMR and IR spectroscopy. The reactions were found to be suitable for calorimetric experiments since they are all rapid, clean and quantitative under experimental calorimetric conditions.

Solution Calorimetry. Calorimetric measurements for reaction between $\text{Ni}(\text{tBu})(\text{CO})_2$ and $\text{Ni}(\text{IAd})(\text{CO})_2$ and phosphine and NHC ligands. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at $120\text{ }^\circ\text{C}$, and then taken into the glovebox. A 15-20 mg sample of $\text{Ni}(\text{tBu})(\text{CO})_2$ or $\text{Ni}(\text{IAd})(\text{CO})_2$ was weighed out accurately into the lower vessel; it was then closed and sealed with 1.5 mL of mercury. Four milliliters of a solution of the ligand of the interest was added. The remainder of a cell was assembled, removed from the glovebox and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organometallic complex was added to the lower vessel. After the calorimeter has reached thermal equilibrium at $30\text{ }^\circ\text{C}$ (approximately 3 h), the calorimeter was inverted, thereby allowing the reactants to mix. After the reaction had reached completion and the calorimeter had once again reached thermal equilibrium (approximately 3 h), the vessels were

removed from the calorimeter, taken into the glovebox, opened, and analyzed using ^1H NMR spectroscopy and IR spectroscopy. The enthalpy of ligand substitution listed in Table 4 and 5 represent the average of 3-5 individual calorimetric determinations with all species in solution.

Enthalpy of Solution of $\text{Ni}(\text{CO})_2(\text{I}^t\text{Bu})$ and $\text{Ni}(\text{CO})_2(\text{IAd})$. In order to consider all species in solution, the enthalpy of solution of $\text{Ni}(\text{CO})_2(\text{I}^t\text{Bu})$ and $\text{Ni}(\text{CO})_2(\text{IAd})$ had to be directly measured. This was performed by using a similar procedure as the one described above, with the exception that no ligand was added to the reaction cell. The enthalpy of solution of $\text{Ni}(\text{CO})_2(\text{I}^t\text{Bu})$, 4.2 ± 0.2 kcal/mol and $\text{Ni}(\text{CO})_2(\text{IAd})$, 2.6 ± 0.2 kcal/mol represent the average of 3-5 individual determinations.

Syntheses. The compounds $\text{Ni}(\text{CO})_2(\text{I}^t\text{Bu})$ and $\text{Ni}(\text{CO})_2(\text{IAd})$ were synthesized according to the literature procedure.¹³ The carbene ligands **1-7** were synthesized following literature procedures.²⁵

$[\text{Ni}(\text{CO})_2(\text{ICy})_2]$ (8**).** Dropwise addition of a pentane solution (20 mL) of ICy (328 mg, 1.44 mmol) to a pentane solution (5 mL) of $\text{Ni}(\text{CO})_2(\text{I}^t\text{Bu})$ (200 mg, 0.677 mmol) under stirring led to a rapid development of a yellow colored solution. The resulting solution was stirred at room temperature for 1 hour. The resulting solution was subsequently concentrated to ca. 10 mL. Cooling the concentrated solution to $-50\text{ }^\circ\text{C}$ resulted in the formation of a yellow precipitate. The solution was filtered and the filtrate was washed with cold pentane (3x5 mL) and dried *in vacuo*. Yield : 310 mg (79%). X-ray quality crystals were grown by slow evaporation of a concentrated pentane solution of complex (**8**). ^1H NMR (C_6D_6 , 400 MHz, δ) 6.1 (s, 4H), 5.0 (m, 4H), 2.2 (m, 8H), 1.62 (m, 8H), 1.46 (d, 5H), 1.40 (m, 8H), 1.22 (m, 8H), 0.9 (m, 4H). ^{13}C NMR (C_6D_6): 205.15 (s), 198.33 (s), 115.77 (s), 5 8.55 (s), 33.77 (s), 25.80 (s). IR ν_{co} (toluene cm^{-1})

1948.6, 1877.9. Anal. Calc. for $C_{32}H_{48}N_4NiO_2$ (MW: 579.45): C, 66.32; H, 8.35; N, 9.66; Found: C, 66.22; H, 8.36; N, 9.65.

[Ni(CO)₂(IMes)₂] (9). A pentane solution (20 mL) of IMes (453 mg, 1.49 mmol) was added dropwise to a pentane solution (5 mL) of Ni(^tBu)(CO)₂ (200 mg, 0.677 mmol). The resulting solution was stirred at room temperature for 1 hour during which time a red precipitate was formed. The solution was subsequently concentrated to ca. 10 mL and then filtered. The solid was washed with cold pentane (-50 °C, 2x5 mL) affording complex **(9)** and dried *in vacuo*. Yield : 356 mg (73 %). ¹H NMR (C₆D₆, 400 MHz, δ) 6.8 (s, 8 H), 6.23 (s, 4 H), 2.11 (s, 12 H), 2.01 (s, 24 H). ¹³C NMR (C₆D₆, 100.6 MHz, δ) 19 8.71 (s), 194.25 (s), 139.07 (s), 135.65 (s), 129.60 (s), 121.96 (s), 21.19 (s), 17.72 (s). IR ν_{co} (toluene, cm⁻¹) 2050.5 (s), 1886.8 (vs). Anal. Calc. For $C_{44}H_{48}N_4NiO_2$ (MW : 723.57): C, 73.03; H, 6.68; N, 7.73. Found: C, 72.96, H, 6.68; N, 7.70.

2.5 References and Notes

- (1) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. J. *Am. Chem. Soc.* **1991**, *113*, 361-363.
- (2) (a) Wanzlik, H.-W. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75-80. For reviews, see: (b) Herrmann, W. A.; Köcher, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2163-2187. (c) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725-728. (d) Arduengo, A. J., III; Krafczyk, R. *Chem. Z.* **1998**, *32*, 6-14. (e) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39-92. (f) Weskamp, T.; Böcher, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12-22. (g) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181-222.
- (3) (a) Parshall, G. W.; Ittel, S. *Homogeneous catalysis*; J. Wiley and Sons: New York, 1992. (b) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal chemistry*; University Science: Mill Valley, CA, 1987. (d) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370-2375. (e) Huang, J.; Jafarpour, L.; Hillier, A. C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 2878-2882. (f) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *17*, 617-618. (g) Weskamp, T. Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2416-2419.
- (4) (a) Herrmann, W. A.; Cornils, B. E. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH : Weinheim, Germany, 1996; Vol. 1; Vol. 2. (b) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93-96. (c) Enders, D.; Gielen, H.; Raabe, G.; Runsink, J.; Teles, J. H. *Chem. Ber.* **1996**, *129*, 1483-1488. (d) Navarro, O.; Kaur, H.; Mahjoor,

P.; Nolan, S. P. *J. Org. Chem.* **2004**, *69*, 3173-3180. (e) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194-16195.

(5) (a) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen. *J. Am. Chem. Soc.* **1999**, *121*, 2674-2678. (b) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *617*, 17-27. (c) Trnka, T. M., Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18-29.

(6) (a) Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. J. *J. Am. Chem. Soc.* **1994**, *116*, 4391-4394. (b) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 9976-9977. (c) MacGuinness, D. S.; Mueller, W.; Wasserscheid, F.; Cavell, K. J.; Skelton, B. W.; White, A. H.; Englert, U. *Organometallics* **2002**, *21*, 175-181.

(7) (a) Omar-Amrani, R.; Thomas, A.; Brenner, E.; Schneider, R.; Fort, Y. *Org. Lett.* **2003**, *5*, 2311-2314. (b) Desmarets, C.; Schneider, R.; Fort, Y. *J. Org. Chem.* **2002**, *67*, 3029-3036. (c) Desmarets, C.; Kuhl, S.; Schneider, R.; Fort, Y. *Organometallics* **2002**, *21*, 1554-1559. (d) Desmarets, C.; Schneider, R.; Fort, Y. *Tetrahedron lett.* **2001**, *42*, 247-250. (e) Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron* **1999**, *55*, 12829-12842.

(8) Sato, Y.; Sawaki, R.; Mori, M. *Organometallics* **2001**, *20*, 5510-5512.

(9) (a) Louie, J.; Gibby, J. E.; Farnworth, M. V. Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188-15189. (b) Zuo, G.; Louie, J. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 2277-2279.

(10) Dible, B. R.; Sigman, M. S. *J. Am. Chem. Soc.* **2002**, *125*, 872-873.

(11) (a) Smith, D. C., Jr.; Haar, C. M.; Stevens, E. D.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G. *Organometallics* **2000**, *19*, 1427-1433. (b) Freeman, S. T. N.; Lemke, F. R.; Haar, C. M.; Nolan, S. P.; Petersen, J. L. *Organometallics* **2000**, *19*, 4828-4833. (c) Laporte, C.; Frison, G.;

Grutzmancher, H.; Hillier, A. C.; Sommer, W.; Nolan, S. P. *Organometallics* **2003**, *22*, 2202-2208. (d) Huang, J.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Inorg. Chem.* **2000**, *39*, 1042-1045. (e) Smith, d. C.; Jr.; Harr, C. M.; Luo, L. C.; Cucullu, M. E.; Mahler, C. H.; Nolan, S. P.; Marshall, W. J.; Jones, N. L.; Fagan, P. J. *Organometallics* **1999**, *18*, 2357-2361. (f) Huang, J.; Schanz, H.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370-2375.

(12) (a) Zhang, C; Huang, J.; Trudell, M.L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804-3805. (b) Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *1*, 9889-9890. (c) Huang, J.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307-1309. (d) Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 119-122. (e) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2000**, *46*, 181-222.

(13) Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S.P. *J. Am. Chem. Soc.* **2003**, *125*, 10490-10491.

(14) Hou, H.; Grantzel, P. K.; Kubiak, C. P. *Organometallics* **2003**, *22*, 2817-2819.

(15) Braga, D.; Grepioni, F.; Orpen, A. G. *Organometallics* **1993**, *12*, 1481-1483.

(16) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdtwek, E.; Scherer, W.; Mink, J. *J. Organomet. Chem.* **1993**, *459*, 177-184.

(17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313-324.

(18) Herrmann, W. A.; Goosen, L. J.; Artus, G. R. J.; Köcher. *Organometallics* **1997**, *16*, 2472-2477.

(19) (a) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357-362. (b) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 4446-4448.

- (20) Tolman, C. A.; Reutter, D. W.; Seidel, W. C. *J. Organomet. Chem.* **1976**, 117, C30-C33.
- (21) Brown, D. L. S.; Connor, J. A.; Skinner, H. A.; *J. Chem. Soc., Faraday I.* **1974**, 70, 1649-1652.
- (22) Eriks, K.; Giering, W. P.; Lui, H. Y.; Prok, A. *Inorg. Chem.* **1989**, 28, 1759-1763.
- (23) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, 92, 2953-2956.
- (24) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, 92, 2956-2965.
- (25) Arduengo, A. J. III; Krafczk, R.; Schmutzler, R.; Craig, H. A.; Georlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, 55, 14523-14534.
- (26) Aresta, M.; Quaranta, E.; Tommasi, I. *J. Chem. Soc. Chem. Comm.* **1988**, 7, 450-452.
- (27) Ballester, L.; Gutierrez-Alonso, A.; Perez-Serrano, S.; Perpignan, M. F. *Inorg. Chem.* **1991**, 30, 2954-2955.

CHAPTER 3

Summary

N-Heterocyclic carbenes have been widely accepted as important ligands in organometallic complexes. They have strong M-NHC bonds and have tunable steric and electronic properties. Thermochemical studies have indicated that 1, 3-disubstituted imidazol-2-ylidene carbene ligands have better electron donating properties than phosphine ligands.

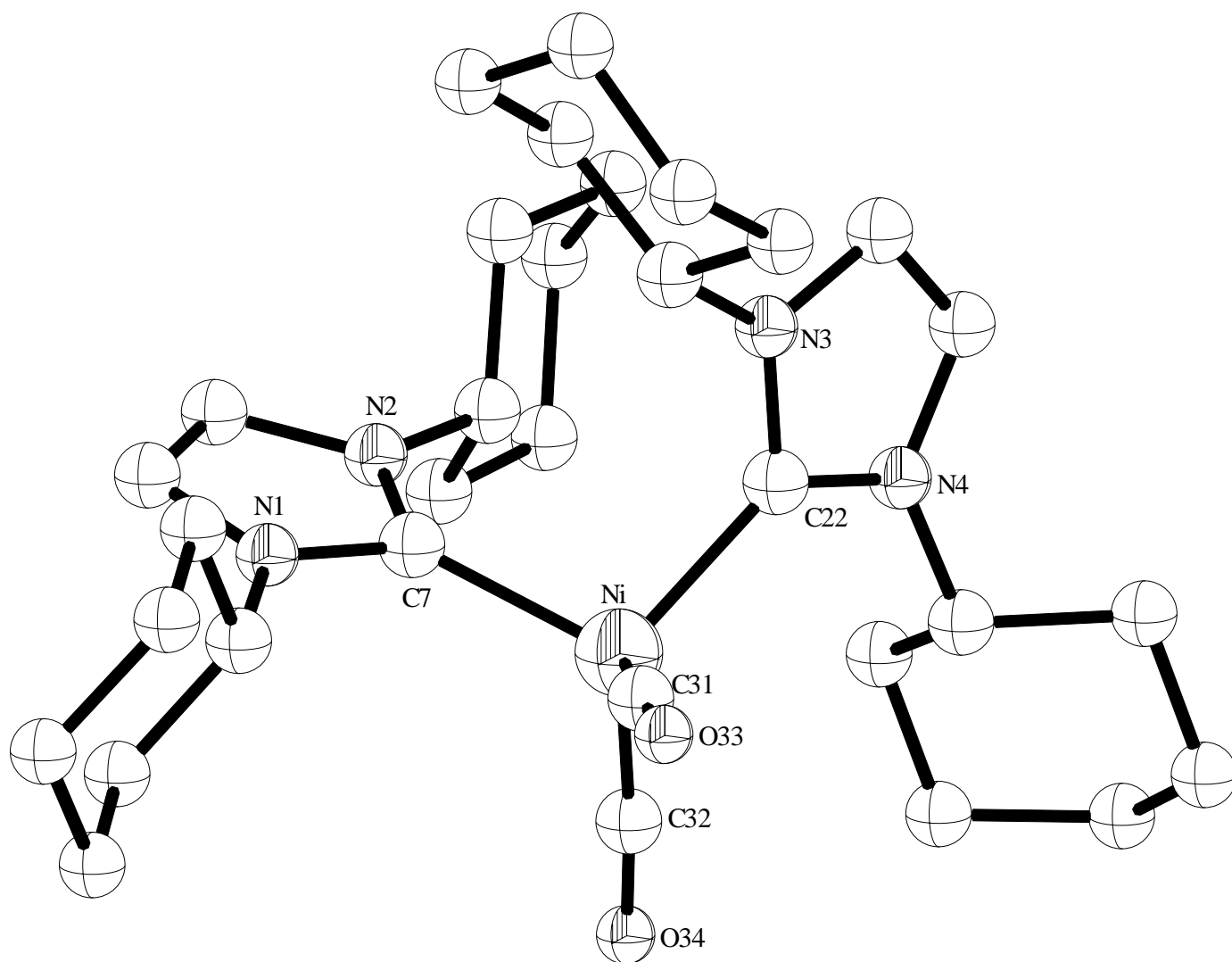
Carbonyl complexes of Ni(0) incorporating two *N*-heterocyclic carbenes of the type Ni(CO)₂(NHC)₂ (NHC = ICy [*N,N'*-bis(cyclohexylimidazol)-2-ylidene], IMes [*N,N'*-bis(2,4,6-trimethylphenyl)-imidazol)-2-ylidene]) have been prepared. The complexes Ni(CO)₂(ICy)₂ and Ni(CO)₂(IMes)₂ have been synthesized and characterized by single crystal X-ray diffraction. The enthalpy of substitution reactions of Ni(CO)₂(NHC) (NHC = I^tBu [*N,N'*-bis(*tert*-butylimidazol)-2-ylidene], IAd [*N,N'*-bis(1-adamentylimidazol)-2-ylidene]) with NHC and tertiary phosphine ligands leading to the formation of Ni(CO)₂(L)₂ (L = NHC, PR₃) complexes have been determined. The solution calorimetric investigations reiterate the greater electron donating property of the NHC ligands compared to tertiary phosphines. Thermochemical studies of the substitution reactions of Ni(CO)₂(NHC) (NHC = I^tBu, IAd) forming complexes Ni(CO)₂(L)₂ (L = NHC, PR₃) led to the determination of average bond dissociation energy of Ni-NHC (NHC = ICy, IMes) and Ni-P (P = PCy₃, PPh₃, P(*p*-Tol)₃, P(*m*-Tol)₃)

APPENDICES

Appendix A

Crystal data and structure refinement for **Ni(CO)₂(ICy)₂**

Empirical formula	C ₃₂ H ₄₈ N ₄ NiO ₂
Formula weight	579.45
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 ₁ /c
Unit cell dimensions	a = 11.1412(18) Å α = 90 deg. b = 18.133(3) Å β = 103.358(2) deg. c = 16.174(3) Å γ = 90 deg.
Volume	3179.1(9) Å ³
Z, Calculated density	4, 1.211 Mg/m ³
Absorption coefficient	0.643 mm ⁻¹
F(000)	1248
Crystal size	0.40 x 0.10 x 0.10 mm
Theta range for data collection	3.61 to 22.50 deg
Limiting indices	-11 ≤ h ≤ 11, -19 ≤ k ≤ 19, -12 ≤ l ≤ 17
Reflections collected / unique	10319 / 4019 [R(int) = 0.0709]



ORTEP drawing of $\text{Ni(CO)}_2(\text{ICy})_2$ (**8**). Selected bond lengths (\AA) and angles (deg): Ni-C(7) 2.023(4), Ni-C(22) 1.991(4), Ni-C(31) 1.789(5), Ni-C(32) 1.762(5), C(31)-O(33) 1.158(5), C(32)-O(34) 1.170(5), C(32)-Ni-C(31) 113.6(2), C(22)-Ni-C(7) 100.95(16).

Absorption correction	Empirical
Max. and min. transmission	23.495 and 3.613
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4019 / 0 / 542
Goodness-of-fit on F^2	1.082
FINAL R INDICES [$I > 2\text{SIGMA}(I)$]	$R1 = 0.0355$, $wR2 = 0.0739$
R INDICES (ALL DATA)	$R1 = 0.0473$, $wR2 = 0.0925$
Largest diff. peak and hole	0.280 and -0.264 e. \AA^{-3}

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **Ni(CO)₂(ICy)₂**

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ni(1)	705(1)	2107(1)	7582(1)	19(1)
N(1)	1145(3)	2067(2)	5782(2)	20(1)
C(1)	2204(4)	2581(3)	5985(3)	22(1)
N(2)	-396(3)	1361(2)	5852(2)	20(1)
C(2)	1932(4)	3292(3)	5475(3)	25(1)
N(3)	1061(3)	498(2)	8005(2)	18(1)
C(3)	3020(5)	3830(3)	5711(4)	29(1)
N(4)	-432(3)	915(2)	8524(2)	17(1)
C(4)	4210(5)	3468(3)	5595(3)	28(1)
C(5)	4492(5)	2761(3)	6121(4)	34(1)
C(6)	3397(4)	2223(3)	5891(4)	30(1)
C(7)	487(4)	1811(2)	6350(3)	19(1)
C(8)	682(4)	1787(3)	4971(3)	26(1)
C(9)	-270(5)	1346(3)	5010(3)	26(1)
C(10)	-1390(4)	954(2)	6136(3)	19(1)
C(11)	-1300(5)	130(3)	5996(4)	30(1)
C(12)	-2342(4)	-296(3)	6272(3)	30(1)
C(13)	-3597(5)	-13(3)	5775(3)	29(1)
C(14)	-3725(4)	814(3)	5921(3)	26(1)
C(15)	-2664(4)	1261(3)	5698(3)	26(1)
C(16)	2244(4)	465(2)	7721(3)	20(1)
C(17)	2209(4)	-64(3)	6986(3)	25(1)
C(18)	3453(4)	-100(3)	6738(3)	26(1)
C(19)	4489(5)	-288(3)	7497(3)	32(1)
C(20)	4543(5)	275(3)	8213(4)	34(1)
C(21)	3307(4)	291(3)	8481(3)	29(1)
C(22)	454(4)	1142(2)	8106(2)	17(1)
C(23)	539(4)	-106(2)	8337(3)	25(1)
C(24)	-388(4)	153(2)	8658(3)	26(1)
C(25)	-1274(4)	1437(3)	8822(3)	21(1)
C(26)	-1545(5)	1182(3)	9673(3)	24(1)
C(27)	-2286(5)	1790(3)	10007(3)	29(1)
C(28)	-3491(5)	1959(3)	9366(3)	33(1)
C(29)	-3259(6)	2159(3)	8491(3)	36(1)

C(30)	-2490(4)	1561(3)	8168(3)	25(1)
C(31)	2213(5)	2426(2)	8095(3)	29(1)
C(32)	-466(5)	2762(2)	7571(3)	37(1)
O(33)	3156(3)	2648(2)	8471(2)	56(1)
O(34)	-1225(4)	3216(2)	7523(3)	73(1)

Table 2. Bond lengths [\AA] and angles [deg] for $\text{Ni}(\text{CO})_2(\text{ICy})_2$

Ni(1)-C(32)	1.762(5)
Ni(1)-C(31)	1.789(5)
Ni(1)-C(22)	1.991(4)
Ni(1)-C(7)	2.023(4)
N(1)-C(7)	1.381(5)
N(1)-C(8)	1.390(5)
N(1)-C(1)	1.480(5)
C(1)-C(6)	1.518(6)
C(1)-C(2)	1.523(6)
N(2)-C(7)	1.384(5)
N(2)-C(9)	1.401(5)
N(2)-C(10)	1.489(5)
C(2)-C(3)	1.535(6)
N(3)-C(22)	1.378(5)
N(3)-C(23)	1.404(5)
N(3)-C(16)	1.493(5)
C(3)-C(4)	1.530(6)
N(4)-C(22)	1.382(5)
N(4)-C(24)	1.397(5)
N(4)-C(25)	1.489(5)
C(4)-C(5)	1.531(7)
C(5)-C(6)	1.539(6)
C(8)-C(9)	1.341(6)
C(10)-C(11)	1.519(6)
C(10)-C(15)	1.536(6)
C(11)-C(12)	1.543(6)
C(12)-C(13)	1.531(7)
C(13)-C(14)	1.530(6)
C(14)-C(15)	1.543(6)
C(16)-C(17)	1.521(6)
C(16)-C(21)	1.530(6)
C(17)-C(18)	1.530(6)
C(18)-C(19)	1.517(7)
C(19)-C(20)	1.534(7)
C(20)-C(21)	1.536(6)
C(23)-C(24)	1.344(6)
C(25)-C(30)	1.531(6)
C(25)-C(26)	1.546(6)
C(26)-C(27)	1.548(6)
C(27)-C(28)	1.525(7)
C(28)-C(29)	1.539(7)
C(29)-C(30)	1.545(6)
C(31)-O(33)	1.158(5)

C(32)-O(34)	1.170(5)
C(32)-Ni(1)-C(31)	113.6(2)
C(32)-Ni(1)-C(22)	114.87(18)
C(31)-Ni(1)-C(22)	107.18(18)
C(32)-Ni(1)-C(7)	104.4(2)
C(31)-Ni(1)-C(7)	115.39(18)
C(22)-Ni(1)-C(7)	100.95(16)
C(7)-N(1)-C(8)	111.6(4)
C(7)-N(1)-C(1)	125.6(3)
C(8)-N(1)-C(1)	122.8(3)
N(1)-C(1)-C(6)	112.3(4)
N(1)-C(1)-C(2)	111.4(4)
C(6)-C(1)-C(2)	112.2(4)
C(7)-N(2)-C(9)	111.1(4)
C(7)-N(2)-C(10)	126.2(3)
C(9)-N(2)-C(10)	122.6(4)
C(1)-C(2)-C(3)	110.9(4)
C(22)-N(3)-C(23)	111.0(3)
C(22)-N(3)-C(16)	124.3(3)
C(23)-N(3)-C(16)	123.9(4)
C(4)-C(3)-C(2)	110.7(4)
C(22)-N(4)-C(24)	111.6(3)
C(22)-N(4)-C(25)	122.9(3)
C(24)-N(4)-C(25)	125.4(3)
C(3)-C(4)-C(5)	111.3(4)
C(4)-C(5)-C(6)	110.4(4)
C(1)-C(6)-C(5)	111.6(4)
N(1)-C(7)-N(2)	103.1(3)
N(1)-C(7)-Ni(1)	127.2(3)
N(2)-C(7)-Ni(1)	129.6(3)
C(9)-C(8)-N(1)	107.3(4)
C(8)-C(9)-N(2)	107.0(4)
N(2)-C(10)-C(11)	111.2(3)
N(2)-C(10)-C(15)	110.6(3)
C(11)-C(10)-C(15)	111.9(4)
C(10)-C(11)-C(12)	111.7(4)
C(13)-C(12)-C(11)	109.7(4)
C(14)-C(13)-C(12)	110.7(4)
C(13)-C(14)-C(15)	112.0(4)
C(10)-C(15)-C(14)	112.2(4)
N(3)-C(16)-C(17)	113.7(4)
N(3)-C(16)-C(21)	109.7(3)
C(17)-C(16)-C(21)	111.9(4)
C(16)-C(17)-C(18)	111.8(4)
C(19)-C(18)-C(17)	111.3(4)

C(18)-C(19)-C(20)	110.5(4)
C(19)-C(20)-C(21)	110.2(4)
C(16)-C(21)-C(20)	110.8(4)
N(3)-C(22)-N(4)	103.3(3)
N(3)-C(22)-Ni(1)	124.9(3)
N(4)-C(22)-Ni(1)	131.1(3)
C(24)-C(23)-N(3)	107.3(4)
C(23)-C(24)-N(4)	106.7(4)
N(4)-C(25)-C(30)	113.1(3)
N(4)-C(25)-C(26)	111.5(3)
C(30)-C(25)-C(26)	109.6(4)
C(25)-C(26)-C(27)	109.1(4)
C(28)-C(27)-C(26)	111.3(4)
C(27)-C(28)-C(29)	111.4(4)
C(28)-C(29)-C(30)	111.7(4)
C(25)-C(30)-C(29)	110.0(4)
O(33)-C(31)-Ni(1)	175.5(4)
O(34)-C(32)-Ni(1)	176.1(4)

Table 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ni(CO)}_2(\text{ICy})_2$
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11 + \dots$

$+2hka^*b^*U12]$

	U11	U22	U33	U23	U13	U12
Ni(1)	25(1)	19(1)	16(1)	0(1)	10(1)	-2(1)
N(1)	18(2)	28(2)	14(2)	-5(2)	6(2)	-11(2)
C(1)	21(3)	34(3)	9(3)	-1(2)	2(2)	-9(2)
N(2)	19(2)	22(2)	20(2)	-8(2)	8(2)	-7(2)
C(2)	18(3)	28(3)	30(3)	4(2)	5(3)	2(2)
N(3)	17(2)	21(2)	19(2)	5(2)	6(2)	-2(2)
C(3)	40(4)	21(3)	28(4)	2(3)	15(3)	-2(3)
N(4)	16(2)	18(2)	20(2)	4(2)	9(2)	-2(2)
C(4)	28(3)	28(3)	29(4)	-3(3)	7(3)	-10(3)
C(5)	28(4)	38(4)	37(4)	3(3)	9(3)	-3(3)
C(6)	27(3)	26(3)	35(4)	9(3)	8(3)	1(3)
C(7)	17(3)	20(3)	21(3)	2(2)	9(2)	3(2)
C(8)	26(3)	38(3)	19(3)	-3(2)	12(3)	-3(2)
C(9)	35(4)	29(3)	16(3)	-6(2)	10(3)	-4(3)
C(10)	16(3)	25(3)	17(3)	1(2)	6(2)	-4(2)
C(11)	25(4)	27(3)	38(4)	3(3)	8(3)	4(2)
C(12)	26(3)	28(3)	36(4)	4(3)	6(3)	-4(3)
C(13)	24(4)	40(3)	26(3)	-3(3)	11(3)	-15(3)
C(14)	14(3)	33(3)	33(3)	-4(3)	7(2)	-7(2)
C(15)	28(3)	27(3)	24(3)	-1(2)	7(3)	0(2)
C(16)	13(3)	25(3)	23(3)	3(2)	7(2)	4(2)
C(17)	27(3)	29(3)	20(3)	2(2)	8(3)	3(3)
C(18)	24(3)	35(3)	21(3)	-6(3)	10(3)	4(3)
C(19)	22(4)	41(4)	36(4)	-1(3)	12(3)	9(3)
C(20)	19(3)	51(4)	28(4)	-1(3)	-2(3)	5(3)
C(21)	28(3)	36(3)	23(3)	-5(3)	9(3)	1(3)
C(22)	19(3)	19(3)	11(3)	-2(2)	-1(2)	1(2)
C(23)	34(3)	13(3)	32(3)	5(2)	15(3)	6(2)
C(24)	27(3)	25(3)	32(3)	5(2)	16(3)	-3(2)
C(25)	21(3)	23(3)	22(3)	-3(2)	10(2)	0(2)
C(26)	26(3)	25(3)	24(3)	1(2)	12(3)	-5(3)
C(27)	39(4)	36(3)	21(3)	-4(3)	21(3)	-2(3)
C(28)	20(3)	40(4)	43(4)	-7(3)	16(3)	1(3)
C(29)	32(4)	51(4)	25(3)	-2(3)	8(3)	17(3)
C(30)	21(3)	41(3)	13(3)	-1(2)	7(2)	5(2)

C(31)	41(4)	34(3)	13(3)	-1(2)	10(3)	-9(3)
C(32)	58(4)	22(3)	39(3)	9(2)	31(3)	3(3)
O(33)	51(3)	70(3)	39(2)	-4(2)	-5(2)	-33(2)
O(34)	86(3)	43(2)	113(4)	31(2)	69(3)	38(2)

Table 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)**Ni(CO)₂(ICy)₂**

	x	y	z	U(eq)
H(1)	2250(40)	2670(20)	6450(30)	26
H(2A)	1790(30)	3198(19)	4790(30)	25(11)
H(2B)	1220(40)	3540(20)	5560(20)	23(12)
H(3A)	3130(30)	3987(19)	6300(20)	16(11)
H(3B)	2880(30)	4300(20)	5420(30)	31(13)
H(4A)	4090(30)	3335(19)	5010(20)	17(12)
H(4B)	4940(40)	3820(20)	5760(20)	35(13)
H(5A)	4590(30)	2885(19)	6650(20)	3(11)
H(5B)	5310(40)	2510(20)	6020(30)	59(15)
H(6A)	3570(30)	1800(20)	6240(20)	25(12)
H(6B)	3280(30)	2046(19)	5300(20)	14(11)
H(8)	1020(40)	1910(20)	4530(30)	29(13)
H(9)	-770(40)	1050(20)	4590(30)	29(13)
H(10)	-1210(30)	1066(18)	6760(20)	16(11)
H(11A)	-1280(30)	-10(18)	5410(20)	7(11)
H(11B)	-510(40)	-80(19)	6310(20)	20(12)
H(12A)	-2240(30)	-840(20)	6210(20)	34(13)
H(12B)	-2250(30)	-203(19)	6950(30)	29(12)
H(13A)	-4260(40)	-250(20)	5930(30)	28(13)
H(13B)	-3670(30)	-113(19)	5180(30)	17(12)
H(14A)	-4550(40)	1040(20)	5580(30)	40
H(14B)	-3730(30)	913(19)	6590(30)	26(11)
H(15B)	-2710(40)	1760(20)	5880(20)	31(13)
H(15B)	2740(30)	1240(20)	5070(30)	28(13)
H(16)	2320(30)	969(19)	7530(20)	18(11)
H(16A)	1540(30)	116(19)	6490(20)	17(11)
H(17B)	1920(30)	-570(20)	7090(20)	25(12)
H(18B)	3400(40)	-460(20)	6330(30)	33(14)
H(18A)	3600(40)	400(20)	6490(30)	48(15)
H(19A)	5290(40)	-303(19)	7370(20)	22(12)
H(19B)	4350(40)	-770(20)	7680(30)	34(14)
H(20A)	5130(40)	133(19)	8680(30)	16(12)
H(20B)	4780(40)	760(20)	8010(30)	34(13)
H(21B)	3310(30)	670(20)	8930(30)	27(12)
H(21A)	3110(30)	-170(20)	8680(20)	16(12)
H(23)	850(30)	-590(20)	8280(20)	14(11)
H(24)	-1010(30)	-107(19)	8930(20)	22(11)

H(25)	-790(30)	1885(19)	8920(20)	12(11)
H(26A)	-1970(30)	740(20)	9600(20)	16(12)
H(26B)	-690(40)	1080(20)	10130(30)	29(12)
H(27A)	-2430(30)	1610(20)	10530(30)	31(13)
H(27B)	-1750(40)	2240(20)	10130(20)	34(14)
H(28A)	-4070(30)	1540(20)	9300(20)	23(12)
H(28B)	-3950(40)	2370(20)	9540(30)	47(15)
H(29A)	-4020(40)	2200(20)	8070(30)	28(13)
H(29A)	-2760(50)	2610(30)	8540(30)	80(20)
H(30A)	-2280(30)	1709(17)	7640(20)	8(10)
H(30B)	-3000(30)	1040(20)	8060(20)	31(12)

Table 5. Torsion angles [deg] for **Ni(CO)₂(ICy)₂**

C(7)-N(1)-C(1)-C(6)	114.6(5)
C(8)-N(1)-C(1)-C(6)	-66.1(5)
C(7)-N(1)-C(1)-C(2)	-118.6(4)
C(8)-N(1)-C(1)-C(2)	60.7(5)
N(1)-C(1)-C(2)-C(3)	178.2(4)
C(6)-C(1)-C(2)-C(3)	-54.9(5)
C(1)-C(2)-C(3)-C(4)	55.6(6)
C(2)-C(3)-C(4)-C(5)	-57.0(6)
C(3)-C(4)-C(5)-C(6)	56.2(6)
N(1)-C(1)-C(6)-C(5)	-178.9(4)
C(2)-C(1)-C(6)-C(5)	54.7(6)
C(4)-C(5)-C(6)-C(1)	-54.8(6)
C(8)-N(1)-C(7)-N(2)	0.2(4)
C(1)-N(1)-C(7)-N(2)	179.5(4)
C(8)-N(1)-C(7)-Ni(1)	-175.3(3)
C(1)-N(1)-C(7)-Ni(1)	4.0(6)
C(9)-N(2)-C(7)-N(1)	0.0(4)
C(10)-N(2)-C(7)-N(1)	-178.0(3)
C(9)-N(2)-C(7)-Ni(1)	175.4(3)
C(10)-N(2)-C(7)-Ni(1)	-2.7(6)
C(32)-Ni(1)-C(7)-N(1)	99.1(4)
C(31)-Ni(1)-C(7)-N(1)	-26.3(4)
C(22)-Ni(1)-C(7)-N(1)	-141.4(3)
C(32)-Ni(1)-C(7)-N(2)	-75.2(4)
C(31)-Ni(1)-C(7)-N(2)	159.4(4)
C(22)-Ni(1)-C(7)-N(2)	44.3(4)
C(7)-N(1)-C(8)-C(9)	-0.4(5)
C(1)-N(1)-C(8)-C(9)	-179.7(4)
N(1)-C(8)-C(9)-N(2)	0.4(5)
C(7)-N(2)-C(9)-C(8)	-0.2(5)
C(10)-N(2)-C(9)-C(8)	177.9(4)
C(7)-N(2)-C(10)-C(11)	-121.4(5)
C(9)-N(2)-C(10)-C(11)	60.8(5)
C(7)-N(2)-C(10)-C(15)	113.6(5)
C(9)-N(2)-C(10)-C(15)	-64.2(5)
N(2)-C(10)-C(11)-C(12)	178.8(4)
C(15)-C(10)-C(11)-C(12)	-54.6(6)
C(10)-C(11)-C(12)-C(13)	58.3(6)
C(11)-C(12)-C(13)-C(14)	58.3(6)
C(12)-C(13)-C(14)-C(15)	55.6(6)
N(2)-C(10)-C(15)-C(14)	175.4(4)
C(11)-C(10)-C(15)-C(14)	50.8(6)
C(13)-C(14)-C(15)-C(10)	-51.5(6)

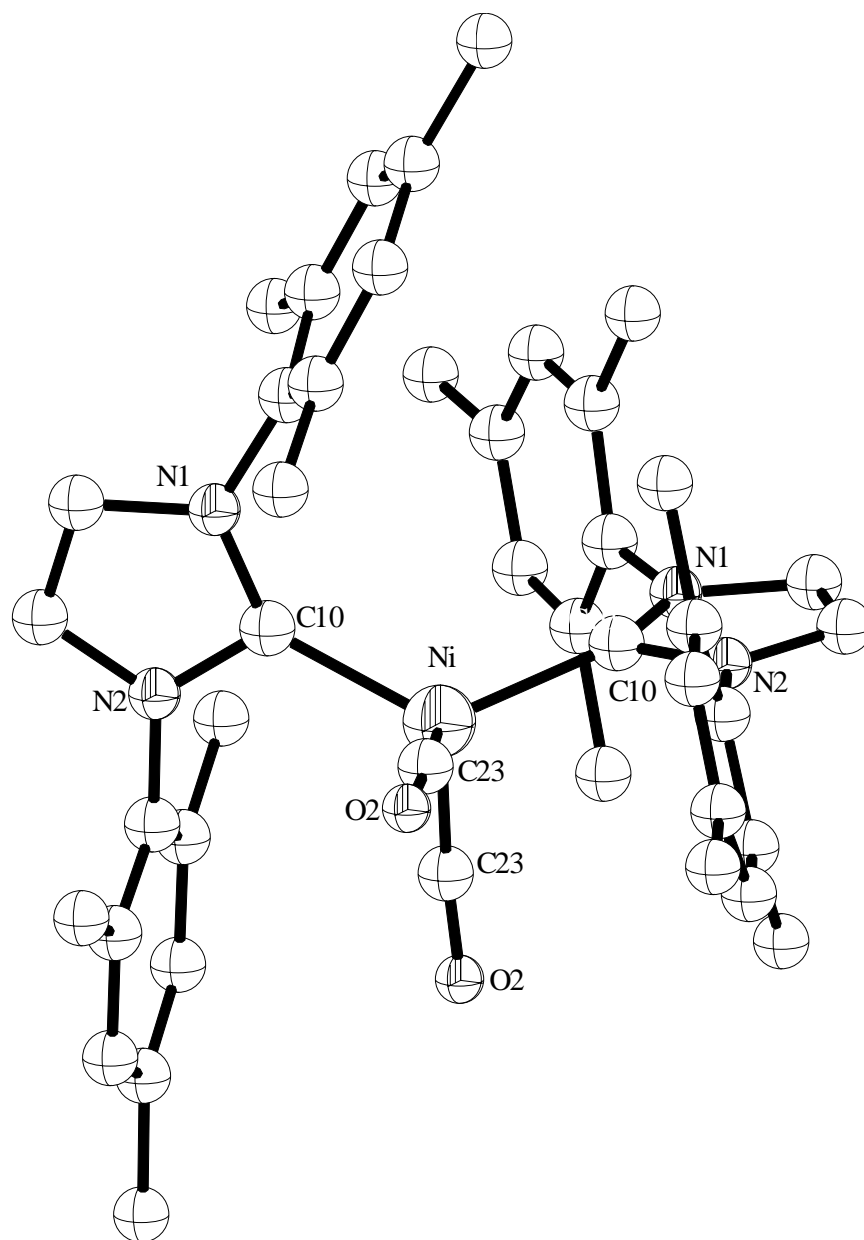
C(22)-N(3)-C(16)-C(17)	-129.0(4)
C(23)-N(3)-C(16)-C(17)	62.2(5)
C(22)-N(3)-C(16)-C(21)	104.9(5)
C(23)-N(3)-C(16)-C(21)	-63.9(5)
N(3)-C(16)-C(17)-C(18)	-178.0(4)
C(21)-C(16)-C(17)-C(18)	-53.1(5)
C(16)-C(17)-C(18)-C(19)	54.4(6)
C(17)-C(18)-C(19)-C(20)	-57.1(6)
C(18)-C(19)-C(20)-C(21)	58.4(6)
N(3)-C(16)-C(21)-C(20)	-178.3(4)
C(17)-C(16)-C(21)-C(20)	54.6(6)
C(19)-C(20)-C(21)-C(16)	-56.9(6)
C(23)-N(3)-C(22)-N(4)	1.2(4)
C(16)-N(3)-C(22)-N(4)	-168.9(3)
C(23)-N(3)-C(22)-Ni(1)	-170.3(3)
C(16)-N(3)-C(22)-Ni(1)	19.6(5)
C(24)-N(4)-C(22)-N(3)	-1.2(4)
C(25)-N(4)-C(22)-N(3)	175.9(3)
C(24)-N(4)-C(22)-Ni(1)	169.5(3)
C(25)-N(4)-C(22)-Ni(1)	13.4(6)
C(32)-Ni(1)-C(22)-N(3)	163.2(3)
C(31)-Ni(1)-C(22)-N(3)	69.5(4)
C(7)-Ni(1)-C(22)-N(3)	51.6(4)
C(32)-Ni(1)-C(22)-N(4)	-5.7(4)
C(31)-Ni(1)-C(22)-N(4)	121.5(4)
C(7)-Ni(1)-C(22)-N(4)	-117.3(4)
C(22)-N(3)-C(23)-C(24)	0.7(5)
C(16)-N(3)-C(23)-C(24)	169.4(4)
N(3)-C(23)-C(24)-N(4)	-0.1(5)
C(22)-N(4)-C(24)-C(23)	0.8(5)
C(25)-N(4)-C(24)-C(23)	-176.2(4)
C(22)-N(4)-C(25)-C(30)	91.8(5)
C(24)-N(4)-C(25)-C(30)	-91.5(5)
C(22)-N(4)-C(25)-C(26)	-144.2(4)
C(24)-N(4)-C(25)-C(26)	32.5(6)
N(4)-C(25)-C(26)-C(27)	173.1(4)
C(30)-C(25)-C(26)-C(27)	-61.0(5)
C(25)-C(26)-C(27)-C(28)	58.4(6)
C(26)-C(27)-C(28)-C(29)	-54.7(6)
C(27)-C(28)-C(29)-C(30)	53.5(6)
N(4)-C(25)-C(30)-C(29)	-175.0(4)
C(26)-C(25)-C(30)-C(29)	60.0(5)
C(28)-C(29)-C(30)-C(25)	-56.2(6)
C(32)-Ni(1)-C(31)-O(33)	48(5)
C(22)-Ni(1)-C(31)-O(33)	-80(5)
C(7)-Ni(1)-C(31)-O(33)	168(5)

C(31)-Ni(1)-C(32)-O(34)	83(7)
C(22)-Ni(1)-C(32)-O(34)	-154(7)
C(7)-Ni(1)-C(32)-O(34)	-44(7)

Appendix B

Crystal data and structure refinement for $\text{Ni(CO)}_2(\text{IMes})_2$

Empirical formula	$\text{C}_{44} \text{H}_{48} \text{N}_4 \text{Ni O}_2$
Formula weight	723.57
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pccn
Unit cell dimensions	$a = 10.7392(6) \text{ Å}$ $\alpha = 90^\circ$ $b = 18.4417(10) \text{ Å}$ $\beta = 90^\circ$ $c = 20.2836(11) \text{ Å}$ $\gamma = 90^\circ$
Volume	$4017.1(4) \text{ Å}^3$
Z, Calculated density	4, 1.196 Mg/m^3
Absorption coefficient	0.523 mm^{-1}
F(000)	1536
Crystal size	0.50 x 0.40 x 0.35 mm
Theta range for data collection	2.21 to 20.00 $^\circ$
Limiting indices	$-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $-19 \leq l \leq 19$
Reflections collected / unique	38689 / 1878 [$R(\text{int}) = 0.0471$]
Completeness to $\theta = 20.00$	9.8 %
Absorption correction	Empirical
Max. and min. transmission	0.969422 and 0.915243



ORTEP drawing for $\text{Ni}(\text{CO})_2(\text{IMes})_2$ (**9**). Selected bond lengths (\AA) and angles (deg): Ni-C(10) 1.983(3), Ni-C(23) 1.761(3), Ni-C(23)-O 1.161(3), C(23)-Ni-C(23) 105.61(18), C(10)-Ni-C(10), 124.22(17).

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1878 / 0 / 323
Goodness-of-fit on F^2	1.135
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0316$, $wR_2 = 0.0607$
R indices (all data)	$R_1 = 0.0345$, $wR_2 = 0.0619$
Extinction coefficient	0.0026(2)
Largest diff. peak and hole	0.160 and -0.179 e. \AA^{-3}

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **Ni(CO)₂(IMes)₂**

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ni(1)	2500	2500	3539(1)	26(1)
N(1)	4245(2)	1617(1)	2631(1)	31(1)
C(1)	3360(3)	1287(2)	2190(2)	31(1)
N(2)	5207(2)	2304(1)	3310(1)	32(1)
O(2)	2038(2)	1314(1)	4457(1)	44(1)
C(2)	2684(3)	681(2)	2384(2)	34(1)
C(3)	1891(3)	375(2)	1920(2)	41(1)
C(4)	1778(3)	633(2)	1284(2)	46(1)
C(5)	2512(4)	1214(2)	1109(2)	50(1)
C(6)	3307(3)	1554(2)	1548(2)	41(1)
C(7)	2790(4)	358(2)	3060(2)	45(1)
C(8)	881(6)	290(3)	801(3)	73(1)
C(9)	4087(5)	2194(2)	1345(2)	60(1)
C(10)	4021(3)	2156(2)	3082(1)	27(1)
C(11)	5506(3)	1448(2)	2585(2)	42(1)
C(12)	6094(3)	1870(2)	3010(2)	45(1)
C(13)	5532(3)	2843(2)	3794(2)	32(1)
C(14)	5680(3)	3559(2)	3595(2)	37(1)
C(15)	6005(3)	4065(2)	4074(2)	46(1)
C(16)	6189(3)	3877(2)	4723(2)	48(1)
C(17)	6062(3)	3155(2)	4895(2)	42(1)
C(18)	5729(3)	2627(2)	4440(2)	37(1)
C(19)	5475(4)	3773(2)	2896(2)	50(1)
C(20)	6515(5)	4436(3)	5241(3)	73(1)
C(21)	5564(4)	1852(2)	4649(2)	48(1)
C(23)	2152(3)	1767(2)	4064(2)	31(1)

Table 2. Bond lengths [Å] and angles [deg] for **Ni(CO)₂(IMes)₂**

Ni(1)-C(23)#1	1.761(3)
Ni(1)-C(23)	1.761(3)
Ni(1)-C(10)	1.983(3)
Ni(1)-C(10)#1	1.983(3)
N(1)-C(10)	1.373(3)
N(1)-C(11)	1.393(4)
N(1)-C(1)	1.440(4)
C(1)-C(2)	1.390(4)
C(1)-C(6)	1.392(4)
N(2)-C(10)	1.383(4)
N(2)-C(12)	1.386(4)
N(2)-C(13)	1.438(4)
O(2)-C(23)	1.161(3)
C(2)-C(3)	1.390(4)
C(2)-C(7)	1.499(5)
C(3)-C(4)	1.381(5)
C(4)-C(5)	1.377(5)
C(4)-C(8)	1.512(6)
C(5)-C(6)	1.383(5)
C(6)-C(9)	1.504(5)
C(11)-C(12)	1.321(5)
C(13)-C(18)	1.386(4)
C(13)-C(14)	1.390(4)
C(14)-C(15)	1.391(5)
C(14)-C(19)	1.489(5)
C(15)-C(16)	1.375(5)
C(16)-C(17)	1.383(5)
C(16)-C(20)	1.512(5)
C(17)-C(18)	1.388(4)
C(18)-C(21)	1.503(5)
C(23)#1-Ni(1)-C(23)	105.61(18)
C(23)#1-Ni(1)-C(10)	110.72(12)
C(23)-Ni(1)-C(10)	102.23(12)
C(23)#1-Ni(1)-C(10)#1	102.23(12)
C(23)-Ni(1)-C(10)#1	110.72(12)
C(10)-Ni(1)-C(10)#1	124.22(17)
C(10)-N(1)-C(11)	112.1(3)
C(10)-N(1)-C(1)	127.2(2)
C(11)-N(1)-C(1)	120.4(3)
C(2)-C(1)-C(6)	121.9(3)
C(2)-C(1)-N(1)	120.5(3)
C(6)-C(1)-N(1)	117.3(3)

C(10)-N(2)-C(12)	111.8(3)
C(10)-N(2)-C(13)	126.0(2)
C(12)-N(2)-C(13)	122.2(3)
C(3)-C(2)-C(1)	117.0(3)
C(3)-C(2)-C(7)	120.3(3)
C(1)-C(2)-C(7)	122.7(3)
C(4)-C(3)-C(2)	123.2(3)
C(5)-C(4)-C(3)	117.3(3)
C(5)-C(4)-C(8)	121.6(4)
C(3)-C(4)-C(8)	121.1(4)
C(4)-C(5)-C(6)	122.7(3)
C(5)-C(6)-C(1)	117.9(3)
C(5)-C(6)-C(9)	121.5(3)
C(1)-C(6)-C(9)	120.6(3)
N(1)-C(10)-N(2)	101.8(2)
N(1)-C(10)-Ni(1)	33.5(2)
N(2)-C(10)-Ni(1)	122.6(2)
C(12)-C(11)-N(1)	106.9(3)
C(11)-C(12)-N(2)	107.4(3)
C(18)-C(13)-C(14)	121.9(3)
C(18)-C(13)-N(2)	118.9(3)
C(14)-C(13)-N(2)	119.1(3)
C(13)-C(14)-C(15)	117.6(3)
C(13)-C(14)-C(19)	120.7(3)
C(15)-C(14)-C(19)	121.6(3)
C(16)-C(15)-C(14)	122.4(3)
C(15)-C(16)-C(17)	117.9(3)
C(15)-C(16)-C(20)	121.7(4)
C(17)-C(16)-C(20)	120.4(4)
C(16)-C(17)-C(18)	122.3(4)
C(13)-C(18)-C(17)	117.8(3)
C(13)-C(18)-C(21)	121.5(3)
C(17)-C(18)-C(21)	120.6(3)
O(2)-C(23)-Ni(1)	171.8(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,z

Table 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **Ni(CO)₂(IMes)₂**
The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2$

$h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ni(1)	18(1)	27(1)	32(1)	0	0	0(1)
N(1)	22(2)	29(2)	41(2)	-2(1)	7(1)	3(1)
C(1)	32(2)	29(2)	32(2)	-5(2)	8(2)	7(2)
N(2)	18(2)	26(2)	53(2)	-1(1)	3(1)	2(1)
O(2)	40(1)	48(1)	45(1)	11(1)	-1(1)	-3(1)
C(2)	35(2)	30(2)	37(2)	-8(2)	3(2)	0(2)
C(3)	48(2)	28(2)	46(3)	-4(2)	10(2)	-2(2)
C(4)	58(2)	42(2)	37(2)	-13(2)	0(2)	14(2)
C(5)	71(3)	52(2)	29(2)	4(2)	4(2)	19(2)
C(6)	48(2)	37(2)	38(2)	1(2)	14(2)	9(2)
C(7)	55(3)	42(2)	39(2)	3(2)	-1(2)	-9(2)
C(8)	87(4)	68(4)	63(4)	-29(3)	-23(3)	11(3)
C(9)	66(3)	60(3)	54(3)	18(3)	17(2)	6(2)
C(10)	27(2)	23(2)	32(2)	6(2)	3(2)	-1(1)
C(11)	33(2)	32(2)	61(2)	-7(2)	16(2)	9(2)
C(12)	21(2)	37(2)	77(3)	-7(2)	4(2)	5(2)
C(13)	13(2)	27(2)	57(2)	-3(2)	0(2)	-2(1)
C(14)	17(2)	32(2)	62(2)	4(2)	5(2)	-1(2)
C(15)	23(2)	24(2)	91(4)	0(3)	5(2)	-4(2)
C(16)	24(2)	45(3)	73(3)	-15(2)	2(2)	-2(2)
C(17)	22(2)	48(3)	56(3)	0(2)	-7(2)	-2(2)
C(18)	17(2)	32(2)	64(3)	2(2)	-1(2)	-1(2)
C(19)	36(3)	42(3)	73(3)	8(2)	3(2)	-2(2)
C(20)	54(3)	67(4)	100(4)	-37(3)	2(3)	-9(3)
C(21)	32(2)	43(3)	70(3)	10(2)	11(2)	-4(2)

Table 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)for **Ni(CO)₂(IMes)₂**

	x	y	z	U(eq)
H(3)	1430(20)	5(14)	2053(12)	15(8)
H(5)	2480(30)	1395(15)	702(15)	43(10)
H(7A)	2900(40)	-1 60(20)	3060(19)	100(15)
H(7B)	3440(30)	519(19)	3294(17)	65(13)
H(7C)	2070(40)	440(20)	3321(19)	91(15)
H(8A)	890(40)	-200(30)	830(20)	98(17)
H(8B)	1100(50)	380(30)	370(30)	130(20)
H(8C)	110(40)	470(20)	850(20)	101(19)
H(9A)	4940(40)	2078(19)	1368(17)	73(13)
H(9B)	3960(30)	2616(19)	1644(16)	64(12)
H(9C)	3900(30)	2317(19)	898(18)	74(13)
H(11)	5790(30)	1078(16)	2294(13)	37(9)
H(12)	6900(30)	1902(15)	3141(14)	37(9)
H(15)	6080(20)	4529(16)	3952(13)	25(8)
H(17)	6230(30)	3001(15)	5343(15)	39(9)
H(19A)	6020(30)	3542(18)	2583(16)	57(11)
H(19B)	4660(40)	3670(17)	2725(16)	61(11)
H(19C)	5600(30)	4280(20)	2829(16)	68(12)
H(20A)	7350(40)	4370(20)	5398(19)	99(16)
H(20B)	5930(40)	4470(20)	5570(20)	90(16)
H(20C)	6480(40)	4890(20)	5070(20)	95(18)
H(21A)	5630(40)	1780(20)	5140(20)	88(14)
H(21B)	4820(30)	1670(18)	4532(16)	58(12)
H(21C)	6170(30)	1530(18)	4455(16)	60(12)

Table 5. Torsion angles [deg] for Ni(CO)₂(IMes)₂

C(10)-N(1)-C(1)-C(2)	-89.6(3)
C(11)-N(1)-C(1)-C(2)	97.0(3)
C(10)-N(1)-C(1)-C(6)	96.7(3)
C(11)-N(1)-C(1)-C(6)	76.7(3)
C(6)-C(1)-C(2)-C(3)	3.7(4)
N(1)-C(1)-C(2)-C(3)	-177.1(3)
C(6)-C(1)-C(2)-C(7)	176.0(3)
N(1)-C(1)-C(2)-C(7)	2.6(4)
C(1)-C(2)-C(3)-C(4)	1.7(5)
C(7)-C(2)-C(3)-C(4)	-178.0(3)
C(2)-C(3)-C(4)-C(5)	1.2(5)
C(2)-C(3)-C(4)-C(8)	-178.7(4)
C(3)-C(4)-C(5)-C(6)	2.3(5)
C(8)-C(4)-C(5)-C(6)	177.6(4)
C(4)-C(5)-C(6)-C(1)	0.4(5)
C(4)-C(5)-C(6)-C(9)	-179.2(3)
C(2)-C(1)-C(6)-C(5)	2.7(4)
N(1)-C(1)-C(6)-C(5)	176.3(3)
C(2)-C(1)-C(6)-C(9)	-177.6(3)
N(1)-C(1)-C(6)-C(9)	-4.0(4)
C(11)-N(1)-C(10)-N(2)	-0.3(3)
C(1)-N(1)-C(10)-N(2)	-174.1(2)
C(11)-N(1)-C(10)-Ni(1)	-163.6(2)
C(1)-N(1)-C(10)-Ni(1)	22.6(4)
C(12)-N(2)-C(10)-N(1)	-0.3(3)
C(13)-N(2)-C(10)-N(1)	179.1(2)
C(12)-N(2)-C(10)-Ni(1)	165.4(2)
C(13)-N(2)-C(10)-Ni(1)	-15.2(4)
C(23)#1-Ni(1)-C(10)-N(1)	-179.6(3)
C(23)-Ni(1)-C(10)-N(1)	68.3(3)
C(10)#1-Ni(1)-C(10)-N(1)	-57.5(2)
C(23)#1-Ni(1)-C(10)-N(2)	19.9(3)
C(23)-Ni(1)-C(10)-N(2)	-92.2(2)
C(10)#1-Ni(1)-C(10)-N(2)	142.0(2)
C(10)-N(1)-C(11)-C(12)	0.7(4)
C(1)-N(1)-C(11)-C(12)	175.0(3)
N(1)-C(11)-C(12)-N(2)	-0.8(4)
C(10)-N(2)-C(12)-C(11)	0.7(4)
C(13)-N(2)-C(12)-C(11)	-178.7(3)
C(10)-N(2)-C(13)-C(18)	99.4(3)
C(12)-N(2)-C(13)-C(18)	-81.3(4)
C(10)-N(2)-C(13)-C(14)	-82.7(4)

C(12)-N(2)-C(13)-C(14)	96.6(3)
C(18)-C(13)-C(14)-C(15)	-1.7(4)
N(2)-C(13)-C(14)-C(15)	-179.5(2)
C(18)-C(13)-C(14)-C(19)	179.4(3)
N(2)-C(13)-C(14)-C(19)	1.6(4)
C(13)-C(14)-C(15)-C(16)	0.6(5)
C(19)-C(14)-C(15)-C(16)	179.5(3)
C(14)-C(15)-C(16)-C(17)	1.0(5)
C(14)-C(15)-C(16)-C(20)	-178.7(3)
C(15)-C(16)-C(17)-C(18)	-1.6(5)
C(20)-C(16)-C(17)-C(18)	178.1(3)
C(14)-C(13)-C(18)-C(17)	1.1(4)
N(2)-C(13)-C(18)-C(17)	178.9(2)
C(14)-C(13)-C(18)-C(21)	179.9(3)
N(2)-C(13)-C(18)-C(21)	- 2.3(4)
C(16)-C(17)-C(18)-C(13)	0.6(5)
C(16)-C(17)-C(18)-C(21)	- 178.2(3)
C(23)#1-Ni(1)-C(23)-O(2)	- 39.0(17)
C(10)-Ni(1)-C(23)-O(2)	76.9(18)
C(10)#1-Ni(1)-C(23)-O(2)	- 148.9(17)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,z

VITA

The author was born in Tallahassee, Florida, U.S.A on December 09, 1977. She graduated from Asieh Senior High School, Shiraz, Iran in July 1997. She began her B.Sc.(Hons. School) at Shiraz University, Shiraz, Iran in September 1997. She graduated from Shiraz University in 2001 with B.Sc.(Hons. School) degree. In the Fall of 2002, she came to the University of New Orleans to pursue an advanced degree in Chemistry under the supervision of Prof. Steven P. Nolan.