Organometallics **2008,** *27,* 3181–3186

Synthetic, Structural, and Thermochemical Studies of N-Heterocyclic Carbene (NHC) and Tertiary Phosphine Ligands in the $[(L)_2Ni(CO)_2]$ ($L = PR_3$, NHC) System

Natalie M. Scott,[‡] Hervé Clavier,[§] Parisa Mahjoor,[‡] Edwin D. Stevens,[‡] and Steven P. Nolan*,[‡,§]

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, and Institute of Chemical Research of Catalonia (ICIQ), Avenida Països Catalans 16, 43007 Tarragona, Spain

Received February 7, 2008

Two new dicarbonyl N-heterocyclic carbene nickel(0) complexes of the type $(NHC)_2Ni(CO)_2$ (NHC = ICy, [*N*,*N*′-bis(cyclohexylimidazol)-2-ylidene (**2**), IMes [*N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol)-2-ylidene] (**3**)) have been prepared by a substitution reaction of $(NHC)Ni(CO)_2$ (NHC = I^tBu [*N*,*N*′-bis(*tert*-butylimidazol)-2-ylidene], IAd [*N*,*N*′-bis(1-adamantylimidazol)-2-ylidene]) and 2 equivalents of ICy or IMes. Single-crystal X-ray analyses confirmed the monomeric 18-electron compositions of $[(ICy)_2Ni(CO)_2]$ (**2**) and $[(IMes)_2Ni(CO)_2]$ (**3**). The greater electron-donating properties of the NHC ligands compared to tertiary phosphines are also demonstrated through calorimetric studies and enabled the determination of average bond dissociation enthalpies for Ni−L (L = NHC and tertiary phosphine).

Introduction

The use of N-heterocyclic carbenes (NHC) as ancillary ligands in organometallic chemistry and homogeneous catalysis is an area of intense activity.[1] On the basis of the accepted analogy between NHCs and trialkylphosphines (strong σ-donors and weak π-accepting ability),[2] many NHC metal complexes are now well recognized as catalysts in a plethora of reactions, including the Suzuki−Miyaura reaction,[3] hydrogenation,[4] and ruthenium-based olefin metathesis.[5] Whereas nickel was used early on to isolate TM-NHC complexes[6] and proved to be useful in catalysis using mostly *in situ* generated catalysts,[7] only a few well-defined NHC Ni(0) complexes have been reported to date. This includes mainly mono-[8] or bis-NHC adducts[6a,9] of nickel carbonyls used for determination of electronic parameters of NHC ligands.

The importance of quantifying steric and electronic effects of ligands has been recognized in pioneering studies by Tolman on tertiary phosphines[10] and have had a major impact on the development of new and improved phosphine ligands for catalysis.[11] Although some spectroscopic studies have revealed the close relationship between NHCs and phosphine ligands,[12] a more detailed understanding of electronic and steric parameters of this ligand class represents a key step for the development of even more catalytic systems.[13] Recent studies on the reactivity of NHC ligands toward complexes containing low-valent transition metals have shown them to be very useful models to understand the strength of metal−ligand bonds.[8c,d] Nevertheless

---

* To whom correspondence should be addressed. E-mail: snolan@iciq.es. Fax: (+34) 977-920-244.

[‡] University of New Orleans.

[§] ICIQ.

(1) For reviews, see: (a) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 725–728. (b) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163–2187. (c) Arduengo, A. J., III; Krafczyk, R. *Chem. Z.* **1998**, *32*, 6–14. (d) Weskamp, T.; Böcher, V. P. W.; Hermmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12–22. (e) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181–222. (f) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (g) Scott, N. M.; Nolan, S. P. *Eur. J. Org. Chem.* **2005**, 1815–1828. (h) *N-heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006. (i) *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Springer-Verlag: Berlin, Germany, 2007. (j) Clavier, H.; Nolan, S. P. *Annu. Rep. Prog. Chem., Sect B: Org. Chem.* **2007**, *103*, 193–222.

(2) (a) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983. (b) 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. (c) Parshall, G. W.; Ittel, S. *Homogeneous Catalysis*; J. Wiley and Sons: New York, 1992. (d) Green, J. C.; Scur, R. G.; Arnold, P. L.; Cloke, G. N. *Chem. Commun.* **1997**, 1963–1964. (e) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370–2375. (f) Huang, J.; Jafarpour, L.; Hillier, A. C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 2878–2882. (g) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *17*, 617–618. (h) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219–224.

(3) (a) Herrmann, W. A.; Cornils, B. E. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, Germany 1996; Vols. *1−2*. (b) Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229–248. (c) Navarro, O.; Kelly, R. A., III.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194–16195. (d) Marion, N.; Ecarnot, E. C.; Navarro, O.; Amoroso, D.; Bell, A.; Nolan, S. P. *J. Org. Chem.* **2006**, *71*, 3816–3821. (e) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101–4111. (f) Navarro, O.; Marion, N.; Mei, J.; Nolan, S. P. *Chem.−Eur. J.* **2006**, *12*, 5142–5148.

(4) (a) Lee, H. M.; Jiang, T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 1255–1258. (b) Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 4246–4252. (c) Vasquez-Serrano, L. D.; Owens, B. T.; Buriak, J. M. *Chem. Commun.* **2002**, 2518–2519. (d) Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D.-R.; Reibenspies, H. J.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 113–123.

(5) (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18–29. (b) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003, Vols. *1−3*. (c) Blechert, S.; Connon, S. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 1900–1923. (d) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592–4633.

(6) (a) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Scherer, W.; Mink, J. *J. Organomet. Chem.* **1993**, *459*, 177–184. (b) Arduengo, A. J.; Gamper, S.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391–4394.

(7) For recent examples, see:(a) Kelly, R. A.; Scott, N. M.; Díez-González, S.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 3442–3447. (b) Lui, L.; Montgomery, J. *J. Am. Chem. Soc.* **2006**, *128*, 5348–5349. (c) Schaub, T.; Backes, M.; Radius, U. *J. Am. Chem. Soc.* **2006**, *128*, 15964–15965. (d) Ho, C.-Y.; Jamison, T. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 782–785. (e) Matsubara, K.; Ueno, K.; Koga, Y.; Hara, K. *J. Org. Chem.* **2007**, *72*, 5069–5076. (f) Schleicher, K. D.; Jamison, T. F. *Org. Lett.* **2007**, *9*, 875–878.

10.1021/om8001125 CCC: \$40.75 © 2008 American Chemical Society
Publication on Web 06/05/2008

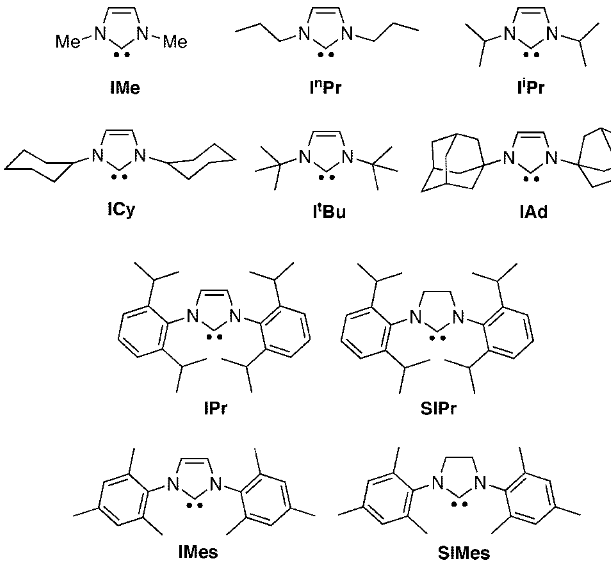


Figure 1. Common saturated and unsaturated NHCs.

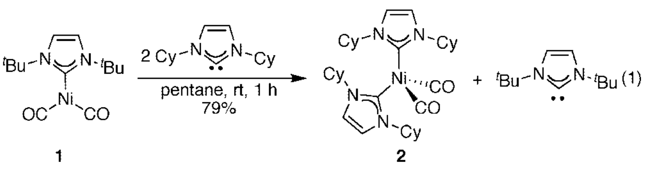
some factors governing the high catalytic activity of many transition metal−NHC complexes remain unclear. In the case of some NHC ligands depicted in Figure 1, surprising differences in catalytic activities of the corresponding metal catalysts have already been observed, but could not be rationalized or explained experimentally.[3d,14]

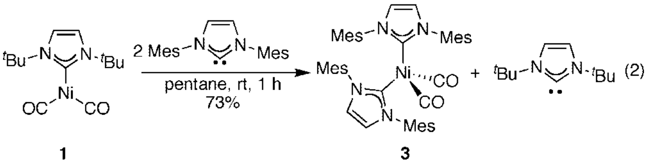
Recently, we reported the synthesis of stable three-coordinate [(NHC)Ni(CO)$_2$] (NHC = ItBu, IAd) and four-coordinate [(NHC)Ni(CO)$_3$] (NHC = ICy, IPr, SIPr, IMes, SIMes) complexes in which the steric and electronic factors governing NHC ligands were investigated in the series of substitution reactions with [Ni(CO)$_4$].[8c,d] It was observed that the formation of three- or four-coordinate complexes was a result of NHC steric bulk and resulting steric congestion around the metal center. While for most NHC ligands one carbonyl group was displaced, generating the saturated [(NHC)Ni(CO)$_3$] species, I^{t}Bu and IAd gave rise to unsaturated [(NHC)Ni(CO)$_2$] compounds, indicating that both ligands are substantially more bulky than P(^{t}Bu)$_3$.

We now employ the dicarbonyl nickel complexes as reagents in reactions involving less bulky NHC ligands, resulting in nickel complexes of the type [(NHC)$_2$Ni(CO)$_2$]. The synthesis, structural characterization, and thermodynamic behavior of complexes of the type [(L)$_2$Ni(CO)$_2$] (L = PR$_3$, NHC) are reported, which enable the determination of Ni−NHC (NHC = ICy, IMes) and Ni−P (P = PCy$_3$, PPh$_3$, P(*p*-Tol)$_3$, P(*m*-Tol)$_3$) bond dissociation energies.

Results and Discussion

Synthesis and Structure Determination of [(ICy)$_2$Ni(CO)$_2$] (2) and [(IMes)$_2$Ni(CO)$_2$] (3). The substitution reaction involving [(I^{t}Bu)Ni(CO)$_2$] (**1**) and 2 equivalents of smaller NHC ligands, such as IMes and ICy, gave rise to the expected saturated complexes of general composition [(NHC)$_2$Ni(CO)$_2$] (eqs 1 and 2) in good isolated yields. Of note, the substitution reactions can also be performed with [(IAd)Ni(CO)$_2$] as starting material to yield **2** and **3** in similar high yields. This synthetic route is original, since [(NHC)$_2$Ni(CO)$_2$] complexes reported to date have been synthesized by double substitution reaction from [Ni(CO)$_4$] using the very small NHC IMe[6a] or by reaction with carbon monoxide from the corresponding [(NHC)$_2$Ni(COD)] complex (NHC = IMes, I^{n}Pr, I^{i}Pr,...; COD = 1,5-cyclooctadiene).[9]





The ^{1}H NMR spectra of complexes **2** and **3** show a characteristic resonance at low field for the two imidazole protons, as well as signals attributable to their corresponding side-chain R groups. The ^{13}C NMR spectra display characteristic low-field resonances for the carbenic carbon at around 190 ppm in addition to one low-field signal for the two carbonyl ligands, indicating that the CO molecules are equivalent. Infrared spectroscopy revealed two ν_{CO} stretching frequencies with the more basic NHC ligand ICy (A$_1\nu_{CO}$ for [(ICy)$_2$Ni(CO)$_2$] = 1948.5 cm^{-1}) exhibiting a better σ-donating capability than IMes (A$_1\nu_{CO}$ for [(IMes)$_2$Ni(CO)$_2$] = 2050.5 cm^{-1}). Elemental analyses also confirmed the compositions of **2** and **3**. To unambiguously establish the structure of complexes **2** and **3**, single-crystal diffraction studies were performed on colorless crystals obtained from cooled (−50 °C), concentrated pentane solutions of **2** and **3**.

ORTEP representations at 50% probability with selected bond distances and angles are shown in Figures 2 (**2**) and 3 (**2**). Complexes **2** and **3** show the expected tetrahedral geometry around the metal center for Ni(0) 18-electron complexes[15] with bond angles between 100° and 115°. A 2-fold rotation axis is present in **3**, with both **2** and **3** having the NHC and carbonyl ligands disposed *cis* to each other. In general, the Ni−C(NHC) distances in **2** and **3** suggest single-bond character and are in good accordance with their almost exclusive σ-donor charac-

---

(8) For mono NHC adducts, see:(a) Lappert, M. F.; Pye, P. L. *Dalton Trans. Inorg. Chem.* **1977**, *21*, 72–80. (b) Hermann, W. A.; Goossen, L. J.; Artus, G. R.; Köcher, J. *Organometallics* **1997**, *16*, 2472–2477. (c) Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490–10491. (d) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485–2495.

(9) Schaub, T.; Radius, U. *Chem.−Eur. J.* **2005**, *11*, 5024–5030. Schaub, T.; Backes, M.; Radius, U. *Organometallics* **2006**, *25*, 4196–4206.

(10) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–324.

(11) (a) Zapf, A.; Ehrentraut, A.; Beller, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4153–4155. (b) Littke, A. F.; Dai, C. Y.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020–4028. (c) Shigeru, S.; Masaaki, Y. *Curr. Org. Chem.* **2007**, *11*, 17–31.

(12) (a) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabree, R. H. *Organometallics* **2003**, *22*, 1663–1667. (b) Kelly, R. A.; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202–210.

(13) For reviews on stereoelectronic parameters of NHCs, see:(a) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–92. (b) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874–883.

(14) For copper-catalyzed hydrosilylation, see:(a) Díez-González, S.; Kaur, H.; Kauer Zinn, F.; Stevens, E. D.; Nolan, S. P. *J. Org.* **2005**, *70*, 4784–4798. For metathesis transformations, see: (b) Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740–5745.

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

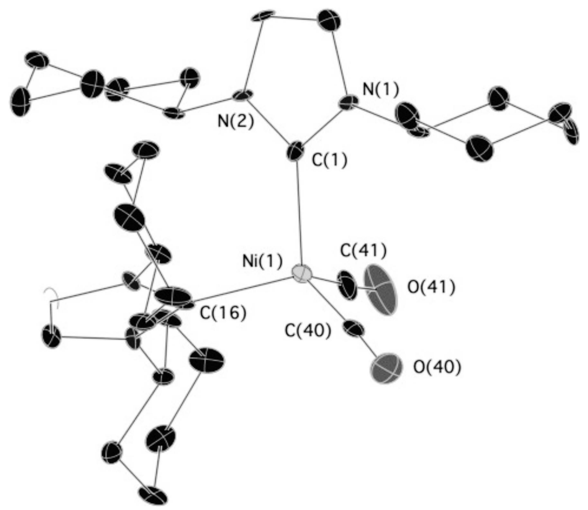


Figure 2. ORTEP diagram of $[(ICy)_2Ni(CO)_2]$ (**2**). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−C(1) 2.021(6), Ni(1)−C(16) 1.997(6), Ni(1)−C(40) 1.796(7), Ni(1)−C(41) 1.755(7), C(40)−O(40) 1.153(6), C(41)−O(41) 1.176(6); C(40)−Ni(1)−C(41) 113.5(3), C(1)−Ni(1)−C(16) 100.9(3), C(1)−Ni(1)−C(40) 115.3(3), C(1)−Ni(1)−C(41) 104.5(2), C(40)−Ni(1)−C(16) 107.3(2), C(41)−Ni(1)−C(16) 114.9(3).

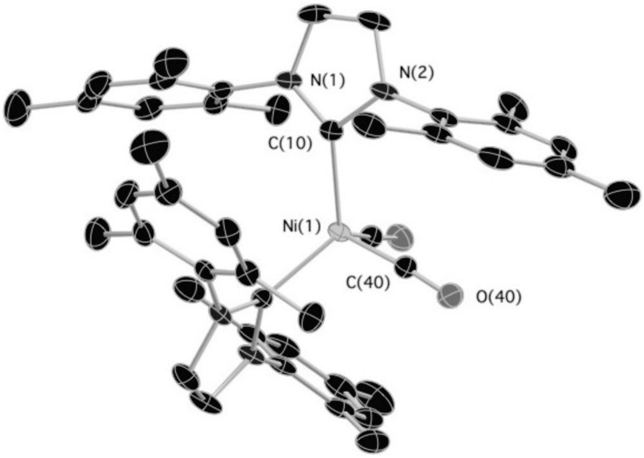


Figure 3. ORTEP diagram of $[(IMes)_2Ni(CO)_2]$ (**3**). Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni(1)−C(1) 1.983(3), Ni(1)−C(40) 1.761(3), C(40)−O(40) 1.161(3); C(1)−Ni(1)−C(1) 124.22(17), C(40)−Ni(1)−C(40) 105.60(18), C(1)−Ni(1)−C(40) 110.72(12), C(40)−Ni(1)−C(1) 102.23(12).

teristics.[16] While the Ni−C(NHC) bond length (1.983(3) Å) in **3** is comparable to analogous distances in related Ni(0) carbene complexes (Table 2),[6a,8b–d,17] **2** possesses one slightly shorter (1.997 Å) and one longer (2.021 Å) Ni−C(NHC) bond length. Since the IR data and enthalpy of reaction measurements (see discussion below) on **2** support that ICy is more strongly bound than IMes, the elongation of the Ni−C(NHC) bond length in **2** may arise simply from crystal packing effects. Furthermore, no significant decrease in the Ni−CO bond length in **2** was observed compared to analogous distances in **3**, and it is similar to other $[(L)Ni(CO)_3]$ systems (Table 2).

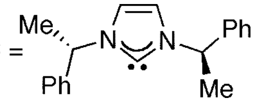
Table 1. Crystallographic Data for Compounds $[(NHC)_2Ni(CO)_2]$

	2	3
emperical formula	$C_{32}H_{48}N_4NiO_2$	$C_{44}H_{48}N_4NiO_2$
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)
α, deg	90	90
β, deg	103.358	90
γ, 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	10 319	38 689
no. of unique data, $l > 2\sigma$	4019	1876
R_{merge}	0.0709	0.0471

Table 2. Selected Bond Lengths (Å) in NHC-Containing Carbonyl Nickel Complexes

entry	complex	$Ni-C_{NHC}$	$Ni-C_{co}$	C−O
1	$[Ni(CO)_4]$[17]		1.817(3)	1.127(3)
2	$[(I^tBu)Ni(CO)_2]$[8c]	1.957(1)	1.7535(13) 1.7489(13)	1.1396(16) 1.1384(16)
3	$[(IAd)Ni(CO)_2]$[8c]	1.953(2)	1.761(2) 1.759(2)	1.147(2)
4	$[(IMe)_2Ni(CO)_2]$[8a]	1.971(4) 1.982(4)	1.757(5) 1.758(5)	1.142(5) 1.152(5)
5	$[(ICy)_2Ni(CO)_2]$, **2**	2.021(4) 1.997(3)	1.775(5)	1.164(5)
6	$[(IMes)_2Ni(CO)_2]$, **3**	1.983(3)	1.791(3)	1.161(3)
7	$[(^iPr)_2Ni(CO)_2]$[9a]	2.002(2)	1.758(2)	1.155(2)
8	$[(NHC)_2Ni(CO)_2]$[8b,a]	1.977(4)	1.758(5)	1.147(5)
9	$[(NHC)Ni(CO)_3]$[8b,a]	1.986(3)	1.794(4)	1.134(5)
10	$[(IPr)Ni(CO)_3]$[8d]	1.972(2)	1.790(3)	1.145(5)
11	$[(IMes)Ni(CO)_3]$[8d]	1.971(3)	1.793(4)	1.144(4)
12	$[(SIPr)Ni(CO)_3]$[8d]	1.962(4)	1.789(4)	1.143(4)
13	$[(SIMes)Ni(CO)_3]$[8d]	1.961(3)	1.780(3)	1.148(3)

[a] NHC =



Calorimetric Results. With the isolation of three- and four-coordinate nickel carbonyl complexes of the type $[(NHC)Ni(CO)_2]$ (NHC = I^tBu, IAd) and $[(NHC)Ni(CO)_3]$ (NHC = ICy, IMes) the equilibrium associated with $[Ni(CO)_4]$ and NHC was found to be crucial in the measurement of Ni−NHC bond dissociation energies.[8b,c] Consequently, we successfully evaluated the bond dissociation energy of Ni with the sterically demanding I^tBu and IAd ligands (BDE for Ni−I^tBu = 39 ± 3 kcal/mol, BDE for Ni−IAd = 43 ± 3 kcal/mol) based on the equilibrium established between three-coordinate $[(NHC)Ni(CO)_2]$ and $[Ni(CO)_4]$. However, we were not successful in establishing an equilibrium between the saturated $[(NHC)Ni(CO)_3]$ (NHC = ICy, IMes) and $[Ni(CO)_4]$. In the present work, we are delighted to report the dissociation energy of the Ni−L bond from the reaction of $[(NHC)Ni(CO)_2]$ (NHC = I^tBu, IAd) with smaller NHC ligands, ICy and IMes, and the substitution reactions involving a variety of tertiary phosphines (PCy_3, PPh_3, $P(p\text{-Tol})_3$, and $P(m\text{-Tol})_3$) with $[(NHC)Ni(CO)_2]$. These data help increase our understanding of the fundamental steric and electronic factors influencing NHC ligands and afford a direct comparison with a large array of tertiary phosphine data.[10] The thermochemistry of $[(PR_3)_2Ni(CO)_2]$ complexes was

---

(16) Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. *Angew. Chem., Int. Ed.* **1995**, *34*, 2371–2374. McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596–1605.

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

Table 3. Enthalpies of Ligand Substitution (kcal/mol) from $[(I^tBu)Ni(CO)_2]^a$

$$[(I^tBu)Ni(CO)_2]_{soln} + 2\ L_{soln} \rightarrow [(L)_2Ni(CO)_2]_{soln}$$

entry	L	$-\Delta H_{rxn}$ (kcal/mol)^b
1	ICy	20.9(0.2)
2	IMes	14.8(0.6)
3	PCy_3	12.6(0.1)
4	P(*p*-Tol)$_3$	11.8(0.3)
5	P(*m*-Tol)$_3$	11.5(0.3)
6	PPh_3	10.7(0.2)

[a] Enthalpy of solution is included. [b] Enthalpy values are reported with 95% confidence limits.

Table 4. Enthalpies of Ligand Substitution (kcal/mol) from $[(IAd)Ni(CO)_2]^a$

$$[(Ad)Ni(CO)_2]_{soln} + 2\ L_{soln} \rightarrow [(L)_2Ni(CO)_2]_{soln}$$

entry	L	$-\Delta H_{rxn}$ (kcal/mol)^b
1	ICy	17.5(0.3)
2	IMes	13.4(0.2)
3	PCy_3	12.0(0.2)
4	P(*p*-Tol)$_3$	11.9(0.3)
5	P(*m*-Tol)$_3$	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.

made possible by the rapid and quantitative reaction of $[(NHC)_nNi(CO)_2]$ (n = 1, 2) with stoichiometric amounts of tertiary phosphine ligands (eq 3).

$$[(NHC)Ni(CO)_2] + 2PR_3 \xrightarrow[\text{toluene, } 30\ ^\circ C]{} [(PR_3)2Ni(CO)_2] + NHC \qquad (3)$$

$$NHC = I^tBu, IAd$$
$$PR_3 = PPh_3, PCy_3, P(p\text{-Tol})_3, P(m\text{-Tol})_3$$

The enthalpy values were determined by anaerobic solution calorimetry in toluene at 30 °C by reacting 2 equiv of either NHC or tertiary phosphine ligands with 1 equiv of $[(NHC)Ni(CO)_2]$ (NHC = I^tBu, IAd). Importantly, the final product of each calorimetric experiment was characterized by NMR spectroscopy in order to exclude other side reactions such as the formation of $[Ni(CO)_4]$ and free NHC. Experimental enthaply data are tabulated in Tables 3 and 4 respectively. Not surprisingly, the magnitude of the enthalpy of reaction is affected by both the steric and electronic nature of the ligands. The NHC ligands ICy (entry 1) and IMes (entry 2) have more exothermic reaction enthalpy than even the very basic tertiary phosphine PCy_3 (entry 3), indicating the greater donor property of these NHC ligands. Interestingly, ICy binds the nickel atom more strongly than IMes, but the gap is generally more important.[2e] Steric factors around the metallic center explain this difference. The tetrahedral geometry of these Ni complexes allows for steric interactions between crowded ligands, and it has been proved that IMes is significantly larger than ICy.[8d,12b] Furthermore, the choice of the phosphine has a significant effect on the reaction outcome. No reaction was observed when reacting the *ortho*-substituted phosphine ligands, tri-*o*-tolylphosphine and tri-*o*-methoxyphenylphosphine, with $[(NHC)Ni(CO)_2]$ (NHC = I^tBu, IAd). However, the reaction readily took place using P(*p*-Tol)$_3$, P(*m*-Tol)$_3$, PCy_3, and PPh_3. The difference in reactivity can be explained by sterics, with the larger tri-*o*-tolylphosphine and tri-*o*-methoxyphenylphosphine ligands (cone angle (θ) = 194 ± 6°[16] and 200°,[18] respectively) not undergoing substitution reactions, while the smaller P(*p*-Tol)$_3$ (θ = 143°), P(*m*-Tol)$_3$ (165°), PCy_3 (170°), and PPh_3 (145°) ligands exhibiting rapid substitiution.[16,19]

Table 5. Bond Dissociation Energies of Ni−NHC and Ni−P^a

entry	L	BDE^{ItBu}	BDE^{IAd}	BDE^{av}
1	ICy	29.9(3.0)	30.2(3.0)	30.1(3.0)
2	IMes	26.9(3.0)	28.2(3.0)	27.5(3.0)
3	PCy_3	25.8(3.0)	27.5(3.0)	26.6(3.0)
4	P(*p*-Tol)$_3$	25.4(3.0)	27.4(3.0)	26.4(3.0)
5	P(*m*-Tol)$_3$	25.2(3.0)	27.0(3.0)	26.1(3.0)
6	PPh_3	24.8(3.0)	26.6(3.0)	25.7(3.0)

[a] BDE^{ItBu}: BDE calculated based on $[(I^tBu)Ni(CO)_2]$ substitution reactions. BDE^{IAd}: BDE calculated based on $[(IAd)Ni(CO)_2]$ substitution reactions. BDE^{av}: average of BDE^{ItBu} and BDE^{IAd}.

As shown in Table 4, the enthalpy values for the reaction of $[(IAd)Ni(CO)_2]$ show a similar pattern as for $[(I^tBu)Ni(CO)_2]$; however, the magnitude of enthalpy of the reaction is marginally smaller. This is a result of the stronger Ni−IAd bond (43 ± 3 kcal/mol) in comparison to the Ni−I^tBu bond (39 ± 3 kcal/mol).

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 reaction for the substitution of $[(I^tBu)Ni(CO)_2]$ with ICy (−20.9 ± 0.2 kcal/mol) or IMes (−14.8 ± 0.6 kcal/mol) and the previously reported bond dissociation energy of Ni−I^tBu (39 ± 3 kcal/mol), these data were used to calculate the bond dissociation energy for Ni−ICy (BDE^{ItBu} for Ni−ICy, 29.9 ± 3.0 kcal/mol) and Ni−IMes (BDE^{ItBu} for Ni−IMes, 26.9 ± 3.0 kcal/mol) (Table 5, entries 1 and 2).[20] Substitution reactions involving $[(IAd)Ni(CO)_2]$ and ICy or IMes give bond dissociation values (BDE^{IAd}) of 30.2 ± 3.0 kcal/mol for Ni−ICy and 28.2 ± 3.0 kcal/mol for Ni−IMes. As shown in Table 5, there is a reasonable agreement between the two values BDE^{ItBu} and BDE^{IAd} obtained for Ni−ICy and Ni−IMes BDEs from respectively $[(I^tBu)Ni(CO)_2]$ and $[(IAd)Ni(CO)_2]$ substitution reactions, which yield an average value (BDE^{av}) of 30.1 ± 3.0 kcal/mol for Ni−ICy and 27.5 ± 3.0 kcal/mol for Ni−IMes bond dissociation energies. The bond strength for Ni−PR_3 was calculated in a similar manner, and the bond dissociation energies are tabulated in Table 5.

Both NHC ligands ICy and IMes possess slightly stronger bond dissociation energies, suggesting that NHC ligands are among the most strongly bound ligands to Ni(0).[21,22] The relative BDE values for Ni−ICy (BDE = 30.1 ± 3.0 kcal/mol) and Ni−IMes (BDE = 27.5 ± 3.0 kcal/mol) are in accordance with the infrared data that indicated that ICy (ν_{CO} for $[(ICy)_2Ni(CO)_2]$ = 1948.6 cm^{-1}) is a better donor than IMes (ν_{CO} for $[(IMes)_2Ni(CO)_2]$ = 2050.5 cm^{-1}). As expected, the strongest nickel−phosphine bond dissociation energy was obtained for the most basic phosphine, PCy_3 (BDE = 26.6 ±

---

(18) (a) Grim, O. S.; Yankowsky, A. W. *J. Org. Chem.* **1977**, *42*, 1236–1239. (b) Pruchnik, F. P.; Smolenski, P.; Wajda-Hermanowicz, K. *J. Organomet. Chem.* **1998**, *570*, 63–69.

(19) Eriks, K.; Giering, W. P.; Lui, H. Y.; Prok, A. *Inorg. Chem.* **1989**, *28*, 1759–1763.

(20) The formula of the calculations is the following: ΔH_{rxn} = [−2 BDE(Ni−L) + BDE(Ni−I^tBu)]; so BDE(Ni−L) = 1/2 [$-\Delta H_{rxn}$ + BDE(Ni−I^tBu)].

(21) (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.

(22) Tolman, C. A.; Reutter, D. W.; Seidel, W. C. *J. Organomet. Chem.* **1976**, *117*, C30−C33.

3.0 kcal/mol, entry 3), while the weakest bond strength (BDE = 25.7 ± 3.0 kcal/mol, entry 6) was found for Ni−PPh_3.

A calorimetric study of the reactions of various phosphorus ligands (and ^{t}BuCN) with $Ni(COD)_2$ by Tolman et al.[22] showed that both the extent of reaction and mean Ni−P bond strengths tend to decrease with increasing ligand size, with $P(OMe)_3$ ($\theta = 107°$)[10,23] having the highest enthalpy value of −57 kcal/mol in the formation of [NiL_4] (L = $P(OMe)_3$). While the reaction of bulky $P(O\text{-}o\text{-}C_6H_4\text{-}^{i}Pr)_3$ ($\theta = 148°$)[10] and [$Ni(COD)_2$] resulted in the formation of [$(L)_2Ni(COD)$] (L = $P(O\text{-}o\text{-}C_6H_4\text{-}^{i}Pr)_3$), it was found to have the lowest enthalpy value of −15 kcal/mol. However, enthalpy values (Table 3) in our system show that BDE of Ni−P in the formation of [$(PR_3)_2Ni(CO)_2$] complexes is dependent on the electron donor−acceptor character of the phosphorus ligand. The decreasing exothermicity in the formation of [$(PR_3)_2Ni(CO)_2$] (PR_3 = PCy_3, P(*p*-Tol)$_3$, P(*m*-Tol)$_3$), PPh_3), which results in a smaller BDE values (Table 5), corresponds closely to the decreasing electron-donating ability of the phosphorus ligand. Nevertheless, only a small difference was observed between the most basic phosphine, PCy_3 (entry 3), and the less donating phosphine, PPh_3 (entry 6). PCy_3 having a larger cone angle ($\theta = 170°$) compared to PPh_3 ($\theta = 145°$)[6a] indicates the overwhelming importance of steric effects in defining the magnitude of the Ni−P bond dissociation energy in this specific nickel system.

Conclusion

The synthesis and structural characterization of [$(ICy)_2Ni(CO)_2$] (**2**) and [$(IMes)_2Ni(CO)_2$] (**3**) is described. We have evaluated the bond dissociation energy of Ni−L associated with the very rapid and quantitative NHC double substitution reactions involving [$(NHC)Ni(CO)_2$] (NHC = I^{t}Bu, IAd) with smaller NHC ligands, ICy and IMes, in addition to reactions involving a variety of tertiary phosphines (PCy_3, PPh_3, P(*p*-Tol)$_3$, P(*m*-Tol)$_3$). The enthalpy values of the formation of [$(L)_2Ni(CO)_2$] (L = ICy, IMes, PCy_3, PPh_3, P(*o*-Tol)$_3$, P(*m*-Tol)$_3$) were measured by solution calorimetry and used to determine Ni−NHC and Ni−P bond dissociation energies. The NHC ligands ICy and IMes were found to have greater electron-donating properties than the most basic tertiary phosphine ligand. Furthermore, an increase in steric bulk (and cone angle for tertiary phosphines) also appears to play a crucial role in the formation of [$(L)_2Ni(CO)_2$] (L = ICy, IMes, PCy_3, PPh_3, P(*p*-Tol)$_3$, P(*m*-Tol)$_3$) complexes and consequently in their bond dissociation energy. This study highlights the intimate relation between electronic and steric parameters and the intrinsic difficulty in separating these.

Experimental Section

General Considerations. All reactions were performed under an inert atmosphere of argon or nitrogen using standard high-vacuum or Schlenk 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 TRIS[8b] reaction or the enthalpy of solution of KCl in water.[21] Experimental enthalpy data are reported with 95% confidence limit. Elemental analysis was performed at Desert Analysis, Tucson, AZ. The compounds [$(I^{t}Bu)Ni(CO)_2$] (**1**) and [$(IAd)Ni(CO)_2$] were synthesized according to the literature procedure.[8c] The NHC ligands were synthesized following literature procedures.[24] Triphenylphosphine (PPh_3), tricyclohexylphosphine (PCy_3), tri-*p*-tolylphosphine (P(*p*-Tol)$_3$), tri-*m*-tolylphosphine (P(*m*-Tol)$_3$), tri-*o*-tolylphosphine (P(*o*-Tol)$_3$), and tri-*o*-methoxyphenylphosphine (P(*o*-MeOPh)$_3$) were used as received (Strem). The identities of nickel phosphine complexes [$(PPh_3)_2Ni(CO)_2$],[25] [$(PCy_3)_2Ni(CO)_2$],[25] [(P(*p*-Tol)$_3$)$_2$Ni(CO)$_2$],[26] and [(P(*m*-Tol)$_3$)$_2$Ni(CO)$_2$][26] were confirmed by comparison with literature spectroscopic data.

Synthesis of [$(ICy)_2Ni(CO)_2$] (2). Dropwise addition of a pentane solution (20 mL) of ICy (328 mg, 1.44 mmol) to a pentane solution (5 mL) of [$(I^{t}Bu)Ni(CO)_2$] (**1**; 200 mg, 0.677 mmol) with magnetic stirring led to a rapid development of a yellow-colored solution. The resulting solution was stirred at room temperature for 1 h. The resulting solution was subsequently concentrated to ca. 10 mL. Cooling the concentrated solution to −50 °C resulted in the formation of a yellow precipitate. The solution was filtered, and the filtrate was washed with cold pentane (3 × 5 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 **2**. Anal. Calcd 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. ^{1}H NMR (C_6D_6, 400 MHz, δ): 6.10 (s, 4H, NCH═C*H*N), 5.00 (m, 4H, CH^{Cy}), 2.20 (m, 8H, CH_2^{Cy}), 1.62 (m, 8H, CH_2^{Cy}), 1.46 (m, 4H, CH_2^{Cy}), 1.40 (m, 8H, CH_2^{Cy}), 1.22 (m, 8H, CH_2^{Cy}), 0.90 (m, 4H, CH_2^{Cy}). ^{13}C NMR (C_6D_6, 400 MHz, δ: 205.15 (N-*C*-N), 198.33 (*C*O), 115.77 (N*C*H═*C*HN), 58.55 (*C*H^{Cy}), 33.77 (*C*H_2^{Cy}), 25.80 (*C*H_2^{Cy}). IR ν_{CO} (toluene, cm^{-1}): 1948.6 (s), 1877.9 (vs).

Synthesis of [$(IMes)_2Ni(CO)_2$] (3). A pentane solution (20 mL) of IMes (453 mg, 1.49 mmol) was added dropwise to a pentane solution (5 mL) of [$(I^{t}Bu)Ni(CO)_2$] (**1**; 200 mg, 0.677 mmol). The resulting solution was stirred at room temperature for 1 h, 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, 2 × 5 mL), affording complex **3**, which was dried *in vacuo*. Yield: 356 mg (73%). Anal. Calcd 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. ^{1}H NMR (C_6D_6, 400 MHz, δ): 6.80 (s, 8 H, CH^{Ar}), 6.23 (s, 4 H, NCH═C*H*N), 2.11 (s, 12 H, CH_3^{Mes}), 2.01 (s, 24 H, CH_3^{Mes}). ^{13}C NMR (C_6D_6, 400 MHz): δ 198.71 (N-*C*-N), 194.25 (*C*O), 139.07 (C^{Ar}), 135.65 (C^{Ar}), 129.60 (*C*H^{Ar}), 121.96 (C^{Ar}), 21.19 (*C*H_3^{Mes}), 17.72 (*C*H_3^{Mes}). IR ν_{CO} (toluene, cm^{-1}): 2050.5 (s), 1886.8 (vs).

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 ^{1}H 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.

Calorimetric Measurements for Reaction of [$(I^{t}Bu)Ni(CO)_2$] or [$(IAd)Ni(CO)_2$] with Tertiary Phosphine and NHC Ligands. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A

---

[23] Bunten, K. A.; Chen, L.; Fernandez, A. L.; Poë, A. J. *Coord. Chem. Rev.* **2002**, 233−23441−51.

[24] Arduengo, A. J.; Krafczk, R.; Schmutzler, R.; Craig, H. A.; Georlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523–14534.

[25] Aresta, M.; Quaranta, E.; Tommasi, I. *J. Chem. Soc., Chem. Commun.* **1988**, *7*, 450–452.

[26] Ballester, L.; Gutierrez-Alonso, A.; Perez-Serrano, S.; Perpinan, M. F. *Inorg. Chem.* **1991**, *30*, 2954–2955.

15−20 mg sample of [(I^{t}Bu)Ni(CO)$_2$] or [(IAd)Ni(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 the 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 °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 NMR and IR spectroscopy. The enthalpy of ligand substitution listed in Tables 2 and 3 represents the average of 3−5 individual calorimetric determinations with all species in solution.

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

The CIF files of crystal structures **2** and **3** have been deposited with the CCDC, No. CCDC-246236 and -246237, respectively. Copies of the data can be obtained free of charge on applications to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033; http://www.ccdc.cam.ac.uk; e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgment. The National Science Foundation is gratefully acknowledged for financial support of this work. N.M.S. thanks the American Australian Education Fund for financial support. S.P.N. (research grant) and H.C. (post-doctoral fellowship) both acknowledge the Ministerio de Educación y Ciencia (Spain) as well as the ICIQ Foundation for support of this work. S.P.N. is an ICREA Research Professor. Dr. Kenneth Moloy and DuPont CR&D are especially thanked for the gift of [Ni(CO)$_4$], as is Eli Lilly and Co. for the generous donation of amines. We are grateful to Professor Carl D. Hoff for his constructive comments.

Supporting Information Available: The CIF files of crystal structures **2** and **3** are available free of charge via the Internet at http://pubs.acs.org.

OM8001125