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Stable, Three-Coordinate $Ni(CO)_2(NHC)$ (NHC = *N*-Heterocyclic Carbene) Complexes Enabling the Determination of Ni−NHC Bond Energies

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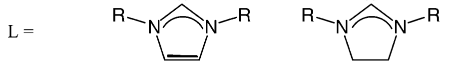
Recent developments in the use of *N*-heterocyclic carbenes (NHC) as ancillary ligands in organometallic chemistry and homogeneous catalysis have drawn attention to this class of compounds as an attractive alternative to the ubiquitous tertiary phosphines.[1] Several beneficial uses of NHC-modified organometallic systems[2] in ruthenium-mediated olefin metathesis,[3] iridium-catalyzed hydrogenation,[4] and palladium cross-coupling[5] chemistry are now well recognized. The most frequently encountered NHCs are presented in Figure 1.



R	L	L
2,4,6-trimethylphenyl	IMes (**1**)	SIMes (**2**)
2,6-diisopropyl	IPr (**3**)	SIPr (**4**)
cyclohexyl	ICy (**5**)	
adamantyl	IAd (**6**)	
tert-butyl	I^{t}Bu (**7**)	

Figure 1. Common unsaturated and saturated NHCs.

To achieve a deeper understanding of the fundamental steric and electronic factors characterizing these ligands and to afford a direct comparison with a large array of tertiary phosphine data,[6] we have carried out a substitution reaction involving NHC ligands with $Ni(CO)_4$.[7] Treating a hexane solution containing IMes (**1**) or SIMes (**2**) with a slight excess of $Ni(CO)_4$ led to evolution of CO and to isolation of the off-white complexes $Ni(CO)_3$(IMes) (**8**) and $Ni(CO)_3$(SIMes) (**9**) in high yield according to eq 1.[8,9] The A_1 carbonyl stretching frequency (cm^{-1}) of complexes **8** and **9** confirms the electron richness of the NHC ligands.[10]

$$Ni(CO)_4 + NHC \rightarrow Ni(CO)_3(NHC) + CO \qquad (1)$$

Surprisingly, when the sterically most demanding IAd (**6**) or I^{t}Bu (**7**) was reacted with $Ni(CO)_4$, we observed formation of orange/red solutions. ^1H and ^{13}C NMR spectral data did not permit unequivocal structural assignment. However, significant infrared shifts to lower frequencies were observed, indicating a possible different composition than $Ni(CO)_3(NHC)$ for these complexes. Indeed, elemental analysis data for the orange microcrystalline materials supported a $Ni(CO)_2(NHC)$ stoichiometry. To unambiguously confirm the structure of these products, single crystals of both complexes were grown by slow evaporation of saturated diethyl ether (for **10**) and pentane (for **11**) solutions. ORTEP diagrams of $Ni(CO)_2$(IAd) (**10**) and $Ni(CO)_2$(I^{t}Bu) (**11**) are presented in Figure 2. Both complexes show only slightly distorted trigonal structures with Ni−C(NHC) bond distances of 1.9528(16) Å (**10**) and 1.9569(11) Å (**11**).[11]

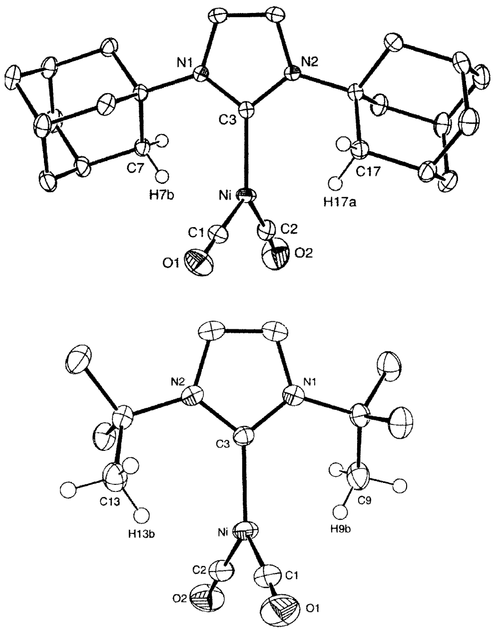


Figure 2. ORTEP views of $Ni(CO)_2$(IAd) (**10**, top) and $Ni(CO)_2$(I^{t}Bu) (**11**, bottom).

These two complexes, isolated in high yields (88% for **10** and 96% for **11**) according to eq 2, are rare examples of three-coordinate nickel carbonyl systems.[12]

$$Ni(CO)_4 + NHC \rightarrow Ni(CO)_2(NHC) + 2CO \qquad (2)$$

To obtain the sought after carbonyl stretching frequencies associated with $Ni(CO)_3$(IAd) and $Ni(CO)_3$(I^{t}Bu), both **10** and **11** were reacted with CO in a high-pressure FTIR cell.[13] Under 1 atm of CO, no significant amount of $Ni(CO)_3(NHC)$ complex is observed even at low temperature. The $Ni(CO)_3(NHC)$ is most likely inherently unstable with respect to disproportionation.[14] Both complexes, **10** and **11**, react with CO to produce $Ni(CO)_4$, the microscopic reverse of eq 2. We reasoned the equilibrium associated with eq 2 could be investigated to afford thermodynamic parameters and allow access to the Ni−NHC (NHC = IAd, I^{t}Bu) bond dissociation energy (BDE). Under equilibrium conditions,[15] a variation of the equilibrium constant can be monitored. Infrared results for IAd are presented in Figure 3.

The van't Hoff plot shows a linear relation ($R^2 = 0.99$) and provides a ΔH of $+10.2 \pm 0.3$ kcal/mol and a ΔS of 41 ± 3 cal/(mol K) for the equilibrium involving IAd. Using the Ni−CO bond energy values for the first and second CO dissociation from $Ni(CO)_4$,[16] a Ni−IAd BDE value of 43 ± 3 kcal/mol is calculated. A similar treatment of the I^{t}Bu complex leads to a Ni−I^{t}Bu BDE value of 39 ± 3 kcal/mol. The relative BDE values are in accord with

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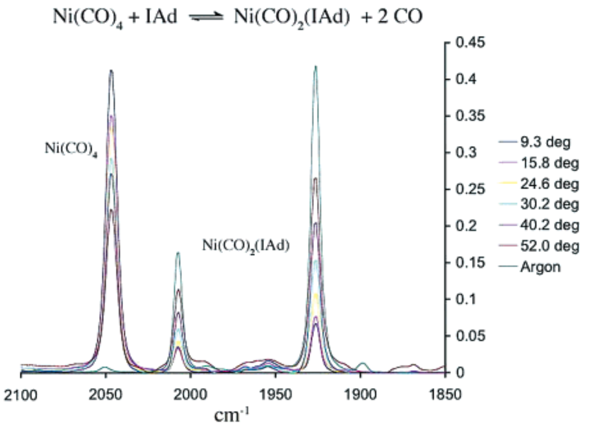

Figure 3. Temperature variation of K_{eq} monitored by FTIR.

the infrared data that indicate that IAd (A_1 ν_{CO} for $Ni(CO)_2(IAd)$ = 2007.2 cm^{-1}) is a better electron donor than I^tBu (A_1 ν_{CO} for $Ni(CO)_2(I^tBu)$ = 2009.7 cm^{-1}). On the basis of the Ni−CO BDE values used in our calculations, the two Ni−NHC BDE values are estimated to be accurate, in an absolute sense, to ±5 kcal/mol.[17] These two Ni−NHC BDEs represent the first experimentally determined report of such values. Noteworthy is the fact that equilibria are not established between the saturated $Ni(CO)_3(NHC)$ complexes and CO, even at elevated pressures of CO.[18] These different reactivity profiles of $Ni(CO)_2(NHC)$ and $Ni(CO)_3(NHC)$ complexes again highlight the very unique nature of complexes **10** and **11**.[19]

Throughout the recent NHC literature, general statements are made about the strength of M−NHC bonds, but none have so far been measured on an absolute basis. Recent accounts of the M−NHC bond being relatively labile have appeared.[20] We suspect that when sterically bulky NHCs are employed, a significant driving force leading to dissociation is a relief of steric pressure around the metal center. This tendency of four-coordinate NiL_4 complexes is well known from the pioneering work of Tolman with phosphine ligands.[6] In the case of the NHC ligands, the presumed $Ni(CO)_3(NHC)$ (NHC = IAd, I^tBu) complexes also display this tendency. Loss of CO yields the unsaturated $Ni(CO)_2(NHC)$ compounds shown in Figure 2. Dissociation of IAd (or I^tBu) establishes the reversible equilibrium shown in Figure 3. More detailed investigations on the reactivity and catalytic uses of complexes **10**, **11**, and their $Ni(CO)_3(NHC)$ congeners are ongoing.

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Supporting Information Available: Experimental procedures, compound characterization, crystallographic and thermochemical data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) CAUTION should be used while manipulating $Ni(CO)_4$ as it is EXTREMELY toxic.

(8) For two examples of related $Ni(CO)_3(NHC)$ complexes, see: (a) Herrmann, W. A.; Goossen, L. J.; Artus, G. R. J.; Köcher, C. *Organometallics* **1997**, *16*, 2472−2477. (b) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Scherer, W.; Mink, J. *J. Organomet. Chem.* **1993**, *459*, 177−184.

(9) Ligands **3**−**5** react in a similar manner. Complete characterization, including X-ray diffraction studies of all of these saturated $Ni(CO)_3(NHC)$ complexes, have been carried out and will be published elsewhere.

(10) For **8**; ν_{CO} (A_1, CH_2Cl_2) = 2050.7 cm^{-1}. For **9**; ν_{CO} (A_1, CH_2Cl_2) = 2051.5 cm^{-1}. For $Ni(CO)_3(P^tBu_3)$; ν_{CO} (A_1, CH_2Cl_2) = 2056.1 cm^{-1}. For less basic phosphines, see ref 6.

(11) (a) An unsaturated, homoleptic Ni(0)−(NHC) complex has been characterized by X-ray crystallography, $Ni(IMes)_2$, showing shorter bond lengths of 1.827 and 1.830 Å, respectively, see: Arduengo, A. J., III; Gamper, S. F.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1994**, *116*, 4391−4394. (b) 1:1 Ni(II)−NHC complexes with Ni−C(NHC) distances of 1.9025(16) and 1.8571(13) Å have been reported recently, see: Dible, B. R.; Sigman, M. S. *J. Am. Chem. Soc.* **2003**, *125*, 872−873.

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(14) Disproportionation was also observed when reacting **10** and **11** with *tert*-butylisoyanide and certain phosphines; unpublished results.

(15) For details, see the Supporting Information.

(16) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 2788−2796 and references cited.

(17) The present result can be compared to a Pd−NHC bond energy of 25.6 kcal/mol recently determined by Cloke and Caddick in a $(NHC)_2Pd(aryl)Cl$ complex: Caddick, S.; Cloke, F. G. N., private communication.

(18) A solution of 39 mg of $Ni(CO)_3(SiMes)$ in 10 mL of heptane (distilled from Na benzophenone under Argon) was prepared in the glovebox and loaded under argon in the high pressure FTIR cell. A spectrum was run under argon, and then the cell was filled with 550 psi CO. A spectrum run immediately after filling, 1 h later, and 1 day later showed no change; in particular, no builidup of $Ni(CO)_4$ at 2046 cm^{-1} was observed during this period. Similar observations were made with $Ni(CO)_3(IMes)$ which also failed to react with CO at 350 psi. See the Supporting Information for spectra.

(19) Initial reactivity studies underline this: electron-poor olefins react with complexes **10** and **11** giving unsaturated, mixed Ni(CO)(NHC)(olefin) compounds. Allyl halides react instantaneously giving rise to carbonyl-free, $Ni^{(II)}(NHC)(allyl)(X)$ complexes. These and related studies will be discussed in detail elsewhere.

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