

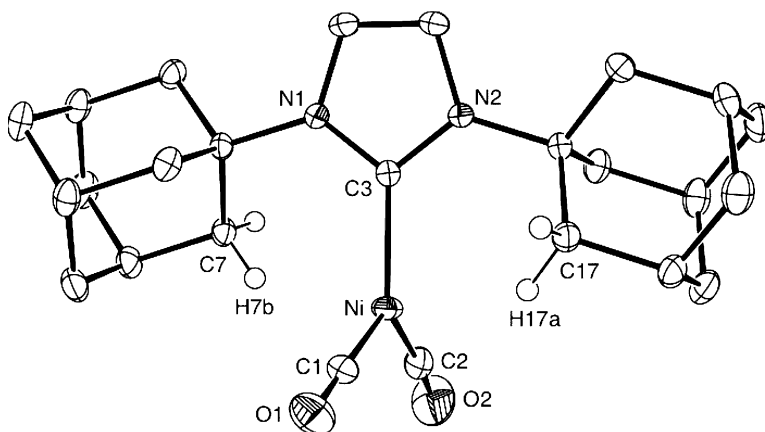
Communication

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## Stable, Three-Coordinate Ni(CO)<sub>2</sub>(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.<sup>1</sup> Several beneficial uses of NHC-modified organometallic systems<sup>2</sup> in ruthenium-mediated olefin metathesis,<sup>3</sup> iridium-catalyzed hydrogenation,<sup>4</sup> and palladium cross-coupling<sup>5</sup> chemistry are now well recognized. The most frequently encountered NHCs are presented in Figure 1.

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,<sup>6</sup> we have carried out a substitution reaction involving NHC ligands with Ni(CO)<sub>4</sub>.<sup>7</sup> Treating a hexane solution containing IMes (1) or SIMes (2) with a slight excess of Ni(CO)<sub>4</sub> led to evolution of CO and to isolation of the off-white complexes Ni(CO)<sub>3</sub>(IMes) (8) and Ni(CO)<sub>3</sub>(SIMes) (9) in high yield according to eq 1.<sup>8,9</sup> The A<sub>1</sub> carbonyl stretching frequency (cm<sup>-1</sup>) of complexes 8 and 9 confirms the electron richness of the NHC ligands.<sup>10</sup>



Surprisingly, when the sterically most demanding IAd (6) or *t*Bu (7) was reacted with Ni(CO)<sub>4</sub>, we observed formation of orange/red solutions. <sup>1</sup>H and <sup>13</sup>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)<sub>3</sub>(NHC) for these complexes. Indeed, elemental analysis data for the orange microcrystalline materials supported a Ni(CO)<sub>2</sub>(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)<sub>2</sub>(IAd) (10) and Ni(CO)<sub>2</sub>(*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).<sup>11</sup>

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.<sup>12</sup>



To obtain the sought after carbonyl stretching frequencies associated with Ni(CO)<sub>3</sub>(IAd) and Ni(CO)<sub>3</sub>(*t*Bu), both 10 and 11 were reacted with CO in a high-pressure FTIR cell.<sup>13</sup> Under 1 atm of CO, no significant amount of Ni(CO)<sub>3</sub>(NHC) complex is observed even at low temperature. The Ni(CO)<sub>3</sub>(NHC) is most

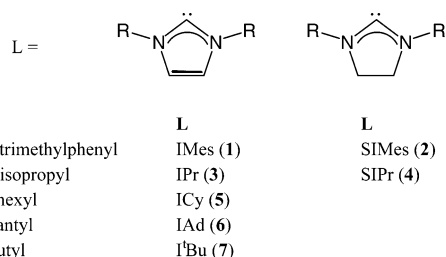


Figure 1. Common unsaturated and saturated NHCs.

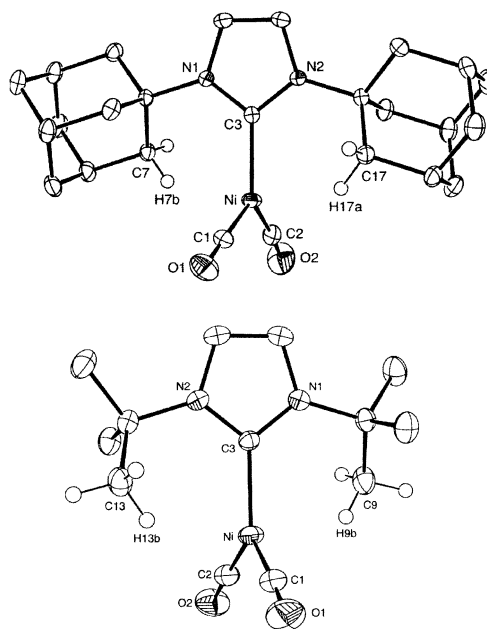


Figure 2. ORTEP views of Ni(CO)<sub>2</sub>(IAd) (10, top) and Ni(CO)<sub>2</sub>(*t*Bu) (11, bottom).

likely inherently unstable with respect to disproportionation.<sup>14</sup> Both complexes, 10 and 11, react with CO to produce Ni(CO)<sub>4</sub>, 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, *t*Bu) bond dissociation energy (BDE). Under equilibrium conditions,<sup>15</sup> 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  $\Delta H$  of  $+10.2 \pm 0.3$  kcal/mol and a  $\Delta S$  of  $41 \pm 3$  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)<sub>4</sub>,<sup>16</sup> a Ni–IAd BDE value of  $43 \pm 3$  kcal/mol is calculated. A similar treatment of the *t*Bu complex leads to a Ni–*t*Bu BDE value of  $39 \pm 3$  kcal/mol. The relative BDE values are in accord with

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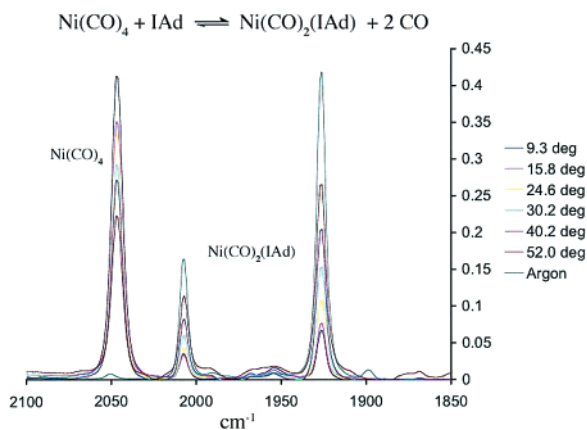


Figure 3. Temperature variation of  $K_{eq}$  monitored by FTIR.

the infrared data that indicate that IAd ( $A_1 \nu_{CO}$  for  $Ni(CO)_2(IAd) = 2007.2 \text{ cm}^{-1}$ ) is a better electron donor than  $tBu$  ( $A_1 \nu_{CO}$  for  $Ni(CO)_2(tBu) = 2009.7 \text{ cm}^{-1}$ ). 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  $\pm 5 \text{ kcal/mol}$ .<sup>17</sup> 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.<sup>18</sup> 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**.<sup>19</sup>

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.<sup>20</sup> 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.<sup>6</sup> In the case of the NHC ligands, the presumed  $Ni(CO)_3(NHC)$  (NHC = IAd,  $tBu$ ) complexes also display this tendency. Loss of CO yields the unsaturated  $Ni(CO)_2(NHC)$  compounds shown in Figure 2. Dissociation of IAd (or  $tBu$ ) 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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- (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**:  $\nu_{CO}$  ( $A_1$ ,  $CH_2Cl_2$ ) = 2050.7  $cm^{-1}$ . For **9**:  $\nu_{CO}$  ( $A_1$ ,  $CH_2Cl_2$ ) = 2051.5  $cm^{-1}$ . For  $Ni(CO)_3(P^tBu_3)$ :  $\nu_{CO}$  ( $A_1$ ,  $CH_2Cl_2$ ) = 2056.1  $cm^{-1}$ . For less basic phosphines, see ref 6.
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- (15) For details, see the Supporting Information.
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- (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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