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Isocyanate and carbodiimide synthesis by nitrene-group-transfer from a nickel(II) imido complex†

Daniel J. Mindiola and Gregory L. Hillhouse*
Searle Chemistry Laboratory, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, USA. E-mail: g-hillhouse@uchicago.edu

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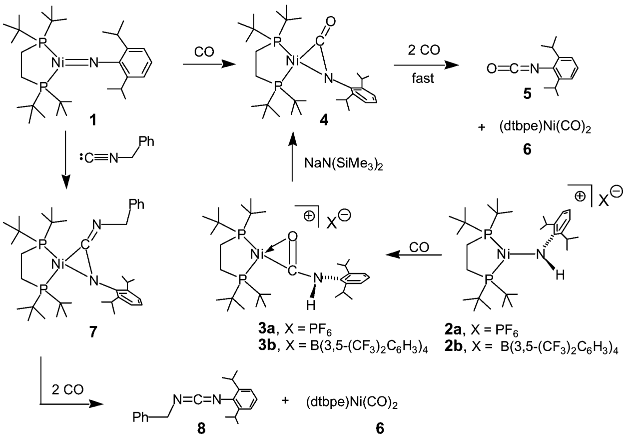
The imido complex (dtbpe)Ni{N(2,6-($CHMe_2$)$_2$$C_6H_3$)} reacts with CO and $CNCH_2Ph$ with addition at the Ni–N bond to give (dtbpe)Ni{*C,N*:η^2-C(O)N(2,6-($CHMe_2$)$_2$$C_6H_3$)} and (dtbpe)Ni{*C,N*:η^2-C(NCH_2Ph)N(2,6-($CHMe_2$)$_2$$C_6H_3$)}; both complexes react further with CO to liberate the isocyanate and carbodiimide ligands with formation of (dtbpe)Ni$(CO)_2$.

The chemistry of transition-metal complexes containing imido ligands (RN^{2-}) is extensive, with these hard, nitrogen-donor ligands exhibiting diverse reactivities ranging from inert "spectator" ligands to very ractive moieties capable of activating hydrocarbon C–H bonds.[1,2] Terminal imido ligands are far more prevalent in complexes of high-valent, early- and mid-transition metals than in complexes of the later-transition elements. The contrast between hard, nitrogen-donor imides and soft, electron-rich late-transition metals has been argued to destabilize the strong π-donor interactions which characterize the bonding of imides in higher-valent compounds.[3] The d^6 iridium imido complexes (η^5-C_5Me_5)Ir≡NR (R = aryl, alkyl, silyl) and the d^6 ruthenium complex (η^6-*p*-cymene)-Ru≡N{2,4,6-(CMe_3)$_3$$C_6H_2$} stood for some time as the only examples of terminal imido complexes possessing a d-electron count greater than four.[4,5] We recently reported the synthesis of a d^8 *nickel imido* complex, (dtbpe)Ni{N(2,6-($CHMe_2$)$_2$$C_6H_3$)} (**1**; dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane), by deprotonation of the amido ligand of [(dtbpe)Ni{NH(2,6-($CHMe_2$)$_2$$C_6H_3$}][$PF_6$] (**2a**).[6] Herein we describe the reactions of carbon monoxide and benzyl isocyanide with the imido ligand of **1** that result in the complete formal nitrene-transfer to CO and C≡NCH_2Ph with elimination of the corresponding isocyanate and carbodiimide products.

Reaction of THF solutions of the cationic amido complex **2a** with an excess of carbon monoxide results in insertion of one equivalent of CO into the Ni–N bond of **2a** to give the carboxyanilide complex salt [(dtbpe)Ni{*C,O*:η^2-OCNH(2,6-($CHMe_2$)$_2$$C_6H_3$)}][$PF_6$] (**3a**) as pale yellow microcrystals in 79% isolated yield (Scheme 1).† **3a** was characterized by elemental analysis and IR (ν_{NH} = 3351, ν_{CO} = 1577 cm^{-1}) and multinuclear NMR (^{1}H, ^{13}C, ^{19}F, ^{31}P) spectroscopy. The ^{1}H NMR resonance for the N*H* proton appears at δ 8.14 (bs s), and inequivalent $-CH_2P(t\text{-}Bu)_2$ arms of the dtbpe ligand are indicated in both the ^{1}H and ^{31}P NMR spectra. The ^{13}C{^{1}H} NMR spectrum of **3**-^{13}C (prepared by reaction of **2a** with ^{13}CO) shows a well-resolved doublet-of-doublets for the carbonyl moiety coupled to two inequivalent phosphorus nuclei (δ 183.2, $^2J_{CP}$ = 10.6, 65.3 Hz), and the IR spectrum of **3**-^{13}C shows the typical isotopic shift for the carbonyl stretch ($\nu_{^{13}CO}$ = 1548 cm^{-1}, $\Delta\nu$ = 29 cm^{-1}). Crystallographic analysis of an analogously prepared tetraarylborate salt, [(dtbpe)Ni{*C,O*:η^2-OCNH(2,6-($CHMe_2$)$_2$$C_6H_3$)}][B(3,5-($CF_3$)$_2$$C_6H_3$)$_4$] (**3b**),‡ confirmed that the carboxyanilide ligand is O,C-bound to Ni (see Fig. 1). Carbon monoxide insertion into late-transition metal–amide bonds has been observed, and there are several examples for Group 10 complexes,[3] including [(η-C_5Me_5)-Ni(μ_2-NHTol)]$_2$ which reacts with CO to give (η-C_5Me_5)-Ni{C(O)NHTol}(CO).[7]

Treatment of a THF solution of **3a** with NaN($SiMe_3$)$_2$ effects deprotonation of **3a** at nitrogen to give the isocyanate complex (dtbpe)Ni{*C,N*-η^2-C(O)N(2,6-($CHMe_2$)$_2$$C_6H_3$)} (**4**) as yellow crystals in 71% isolated yield Scheme 1).† The IR spectrum of **4** shows no N–H stretch and a strong ν_{CO} at 1719 cm^{-1}. The higher carbonyl stretching vibration in neutral **4** relative to cationic **3a** ($\Delta\nu$ = 142 cm^{-1}) suggests that the isocyanate ligand is coordinated to Ni in an η^2:*C,N* fashion in **4**. An X-ray diffraction study on crystals of **4**, although disordered, also confirms this connectivity.[8]† Elemental analysis and multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) support this formulation. When the deprotonation reaction is monitored by NMR



3a, X = PF_6
3b, X = B(3,5-(CF_3)$_2$$C_6H_3$)$_4$
2a, X = PF_6
2b, X = B(3,5-(CF_3)$_2$$C_6H_3$)$_4$

Scheme 1

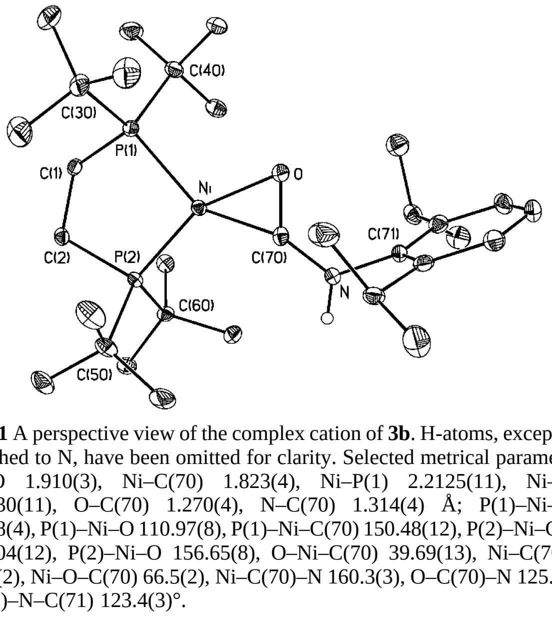


Fig. 1 A perspective view of the complex cation of **3b**. H-atoms, except that attached to N, have been omitted for clarity. Selected metrical parameters: Ni–O 1.910(3), Ni–C(70) 1.823(4), Ni–P(1) 2.2125(11), Ni–P(2) 2.1530(11), O–C(70) 1.270(4), N–C(70) 1.314(4) Å; P(1)–Ni–P(2) 92.08(4), P(1)–Ni–O 110.97(8), P(1)–Ni–C(70) 150.48(12), P(2)–Ni–C(70) 117.04(12), P(2)–Ni–O 156.65(8), O–Ni–C(70) 39.69(13), Ni–C(70)–O 73.8(2), Ni–O–C(70) 66.5(2), Ni–C(70)–N 160.3(3), O–C(70)–N 125.7(3), C(70)–N–C(71) 123.4(3)°.

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† Electronic supplementary information (ESI) available: complete experimental, spectroscopic, analytical, and crystallographic details. See http://www.rsc.org/suppdata/cc/b2/b204846a/

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spectroscopy (^{1}H, ^{13}C, ^{31}P), an intermediate whose spectra are consistent with the *C*,*O*:η^2-isocyanate isomer is observed and it cleanly converts to **4** over a period of several hours.

Treatment of a Et_2O solution of the neutral Ni(II) imido complex **1** with carbon monoxide (1 atm, 22 °C) results in a color change from emerald-green to pale yellow over a 2 h period with formation of the free arylisocyanate O=C=N(2,6-$(CHMe_2)_2C_6H_3$) (**5**) along with the Ni(0) dicarbonyl complex (dtbpe)Ni$(CO)_2$ (**6**),[9] depicted in Scheme 1.† The carbonylation of **1** gives **5** and **6** quantitatively, as determined by ^{1}H NMR integration against an internal standard (**6** was isolated from the reaction mixture as tan crystals in 60% yield). Identification of **5** as *o*-diisopropylphenyl isocyanate was supported by GC/MS analysis of the reaction mixture (m/z = 203, M$^+$) as well as by spectroscopic comparison with an authentic sample. Reaction of **1** with 1 equivalent of CO gives a mixture containing unreacted **1** along with **4**, **5** and **6** (as determined by IR and multinuclear NMR spectroscopy), strongly implicating **4** as an intermediate in the carbonylation reaction of **1** that gives **5** and **6**; the subsequent reaction of **4** with CO is fast with respect to the initial formation of **4** (Scheme 1). Consistent with this mechanism, addition of CO to a solution of pure **4** gives **5** and **6** rapidly and quantitatively.

The coordination chemistry of isocyanides often parallels that of the isolobal CO molecule, and in a reaction related to that observed with carbon monoxide, treatment of cold (−35 °C) diethyl ether solutions of **1** with benzyl isocyanide results in addition of $C{\equiv}NCH_2Ph$ across the Ni–N double bond to give the unsymmetrical carbodiimide adduct (dtbpe)Ni{*C*,*N*:η^2-C(NCH_2Ph)N(2,6-$(CHMe_2)_2C_6H_3$)} (**7**) as pale-pink crystals in 50% yield (Scheme 1).† NMR data (^{1}H, ^{13}C, ^{31}P) are typical for square-planar Ni(II) and a strong ν_{CN} is observed in the IR spectrum at 1684 cm^{-1}. The solid-state structure of **7** was crystallographically determined, and a view of the molecule is shown in Fig. 2.‡ We see no evidence in solution for isomers, *i.e.*, binding of the carbodiimide ligand through the benzylic-CN bond. Unlike the reaction of **1** with CO, excess benzyl isocyanide does not displace the carbodiimide ligand. However, exposure of **7** to an excess of CO results in elimination of the carbodiimide $PhCH_2N{=}C{=}N$\{2,6-$(CHMe_2)_2C_6H_3$\} (**8**; GC/MS, m/z = 292, M$^+$) and formation of **6** (Scheme 1). It is noteworthy that the reaction of **7** with CO is not as clean as that of **4** with CO (to give **5**). ^{1}H NMR and IR analyses indicates **8** is formed in ~ 50% yield with substantial decomposition of **7** to give free benzyl isocyanide also occurring.

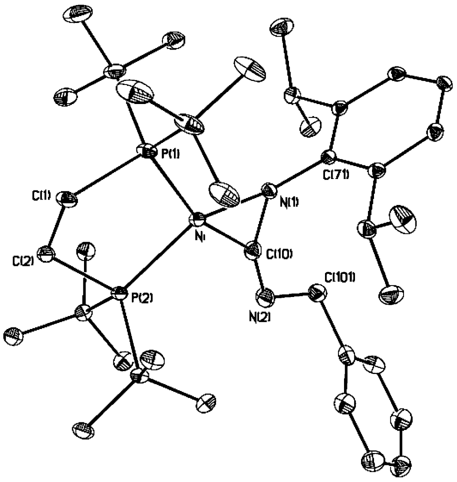

Fig. 2 A perspective view of the molecular structure of **7**. H-atoms have been omitted for clarity. Selected metrical parameters: Ni–N(1) 1.879(2), Ni–C(10) 1.857(2), Ni–P(1) 2.2360(6), Ni–P(2) 2.1517(6), N(1)–C(10) 1.318(3), N(1)–C(71) 1.411(3), N(2)–C(10) 1.275(3), N(2)–C(101) 1.474(3) Å; P(1)–Ni–P(2) 92.93(2), P(1)–Ni–N(1) 121.07(6), P(1)–Ni–C(10) 162.35(8), P(2)–Ni–C(10) 104.63(8), P(2)–Ni–N(1) 144.97(6), N(1)–Ni–C(10) 41.32(9), Ni–C(10)–N(1) 70.22(13), Ni–N(1)–C(10) 68.46(13), Ni–C(10)–N(2) 144.3(2), N(1)–C(10)–N(2) 145.5(2), C(10)–N(2)–C(101) 119.1(2), C(10)–N(1)–C(71) 134.5(2)°.

It is notable that for low-valent early-metals (*e.g.*, $WCl_2(PMePh_2)_4$), thermodynamics favour interactions of isocyanates and carbodiimides in the reverse sense of the reactions reported herein, that is they oxidatively add to give stable imido–carbonyl and imido–isocyanide complexes such as W(NR)Cl_2(CO)$(PMePh_2)_2$ and W(NR)Cl_2(CNR)$(PMePh_2)_2$.[10] Although late-metal terminal imido complexes are quite rare, (η^5-C_5Me_5)Ir≡NR has been shown to react with CO and C≡NR *via* addition accross the Ir–N bond to give 18-electron species (η^5-C_5Me_5)Ir(CO)(RNCO) and (η^5-C_5Me_5)Ir(CNR)(RNCNR). These compounds, however, are apparently stable with respect to complete nitrene-group transfer with reductive elimination to give the metal-free heterocumulenes,[4] although free carbodiimide formation has been observed in the reaction of an isocyanide with a tantalum imido complex.[11]

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Notes and references

‡ *Crystal data* for **3b**·2Et_2O, $C_{69}H_{80}BF_{24}NNiO_{2.5}P_2$: triclinic, $P\bar{1}$, a = 12.495(3), b = 16.167(4), c = 18.487(4) Å, α = 98.050(2), β = 91.659(4), γ = 91.399(4), Z = 2, μ(Mo-Kα) = 0.410 mm^{-1}. Of 17173 total reflections (yellow block, 1.27 ⩽ θ ⩽ 24.00°), 11460 were independent and observed (R_{int} = 4.09%) with $I > 2\sigma(I)$. A semi-empirical absorption correction was performed using psi-scans. Direct methods were used to locate Ni, P, O, N, F, B, and C atoms from the E-map. No anomalous bond lengths or thermal parameters were noted except for one disordered diethyl ether molecule of solvation which resided at an inversion centre (O2S). One peripherical CF_3 group of the counter-anion suffered from disorder but converged normally during refinement. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically and fit to idealised positions. GoF on F^2 = 1.069; $R(F)$ = 5.98% and $R(wF)$ = 15.03%. *Crystal data* for **7**, $C_{38}H_{64}F_6N_2NiP_2$: monoclinic, P2$_1$/n, a = 10.8143(7) Å, b = 17.9376(12) Å, c = 19.3299(14) Å, β = 100.1160(10)°, Z = 4, μ(Mo Kα) = 0.640 mm^{-1}. Of 22171 total reflections (pink prism, 2.02 = θ = 28.27°), 8619 were independent and observed (R_{int} = 4.81%)with $I > 2\sigma(I)$. A semi-empirical absorption correction was performed using psi-scans. Direct methods were used to locate the Ni, P, N, and C atoms from the E-map. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically and fit to idealised positions. No anomalous bond lengths or thermal parameters were noted. GoF on F^2 = 1.114; R(F) = 5.02% and R(wF) = 12.02%. CCDC reference numbers 186268–186270. See http://www.rsc.org/suppdata/cc/b2/b204846a/ for crystallographic data in CIF or other electronic format.

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