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An Anionic Zerovalent Nickel Carbonyl Complex Supported by a Triphosphine Borate Ligand: An Ni−C≡O−Li Isocarbonyl

Hongyi Hou, Arnold L. Rheingold,[†] and Clifford P. Kubiak*

Department of Chemistry and Biochemistry, University of California at San Diego,
9500 Gilman Drive, La Jolla, California 92093-0358

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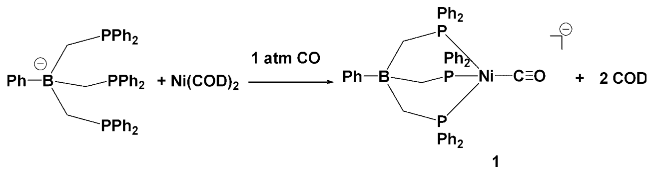
An anionic zerovalent nickel carbonyl complex, [Ni(PhBP$_3$)(CO)][Li(TMED)] (**1**), supported by a triphosphine borate ligand was prepared and structurally characterized. The solid state structure shows the coordination of Li$^+$ to the O atom of the CO ligand. The isocarbonyl structure indicates strong electron donor ability of the [PhBP$_3$] ligand and charge redistribution to the carbonyl oxygen. Results of a DFT calculation support this view. Complex **1** represents the first example of a Lewis acid O atom adduct of a Ni(0) carbonyl complex.

Introduction

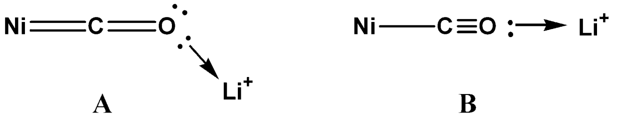
The anionic transition metal carbonyls (carbonylates) have been extensively studied with regard to their interactions with main group metal cations and Lewis acids in solid state and solution.[1,2] Besides their synthetic and catalytic applications, the transition metal carbonylates have served as models for the biological systems that exhibit bifunctional (acidic-basic) activation of small molecules such as CO, NO, N$_2$, and CO$_2$.[3] A better understanding of the basic principles behind the solvent, cation, and ancillary ligand effects on organometallic ion pairing is thus an important goal.

Burlitch and co-workers reported studies of the CO stretching frequencies in the tungsten carbonyl anion [CpW(CO)$_3$]$^-$ system, in which both the metal center and the carbonyl oxygen could be sites of Lewis basicity, depending on the nature of the Lewis acid added.[4−6] Shriver and co-workers demonstrated the coordination of alkyl aluminum reagents to the bridging carbonyl oxygen in an iron carbonyl complex.[7] Darensbourg et al. have examined in detail the factors including solvent polarity, cation electrostatic potential, cation solvation, and the phosphine ligand cone angle that affect ion contact site selection of alkali cation contact ion pairs with anionic transition metal hydrides and carbonylates.[8−10]

Scheme 1. Synthesis of Complex [Ni(PhBP$_3$)(CO)][Li(TMED)] (1)



Scheme 2. Valence Bond Structures of Complex [Ni(PhBP$_3$)(CO)][Li(TMED)] (1)



The anionic tridentate phosphine ligand [PhB(CH$_2$PPh$_2$)$_3$]$^-$ (herein abbreviated as [PhBP$_3$]) was reported in 1999.[11,12] The incorporation of a negative charge into the ligand framework adjacent to the "soft" phosphine donor groups attracted our attention. A question of particular interest is how the donating ability of the ligand is affected by charge redistribution after binding to a metal center. Here we report the preparation and structure of an Ni−C≡O−Li isocarbonyl formed by coordination of Li$^+$ to the O atom of the CO ligand of an anionic nickel(0) carbonyl complex with the [PhBP$_3$] ligand.

Results and Discussion

The complex [Ni(PhBP$_3$)(CO)][Li(TMED)] (**1**) was obtained straightforwardly by reaction of [Li(TMED)][PhB(CH$_2$PPh$_2$)$_3$][12] with Ni(COD)$_2$[13] (COD = 1,5-cyclooctadiene) under 1 atm CO at room temperature (Scheme 1). This contrasts with the apparent difficulty in prepar-

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* To whom correspondence should be addressed. E-mail: ckubiak@ucsd.edu.

[†] Address correspondence pertaining to crystallographic studies to this author. E-mail: arheingold@ucsd.edu.

(1) Edgell, W. F. *Ions Ion Pairs Org. React.* **1972**, *1*, 153−176.
(2) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221−274.
(3) Floriani, C. *Pure Appl. Chem.* **1983**, *55*, 1−10.
(4) Burlitch, J. M.; Petersen, R. B. *J. Organomet. Chem.* **1970**, *24*, C65−C67.
(5) Burlitch, J. M.; Petersen, R. B.; Stezowski, J. J.; Wan, C. n.; Hughes, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 3532−3533.
(6) Ulmer, S. W.; Skarstad, P. M.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 4469−4471.
(7) Nelson, N. J.; Kime, N. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1969**, *91*, 5173−5174.
(8) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521−1530.
(9) Kao, S. C.; Darensbourg, M. Y.; Schenk, W. *Organometallics* **1984**, *3*, 871−876.
(10) Ash, C. E.; Delord, T.; Simmons, D.; Darensbourg, M. Y. *Organometallics* **1986**, *5*, 17−25.
(11) Barney, A. A.; Heyduk, A. F.; Nocera, D. G. *Chem. Commun.* **1999**, 2379−2380.
(12) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871−9872.
(13) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5−9.

10.1021/om049601f CCC: $30.25

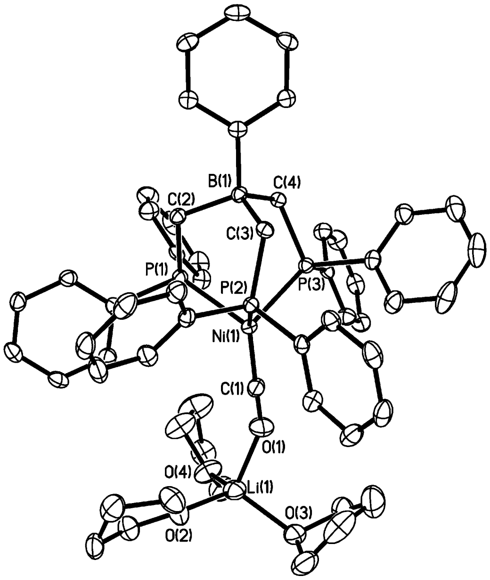

Figure 1. ORTEP view of $[\mathrm{Ni(PhBP_3)(CO)}][\mathrm{Li(THF)_3}]$ (**1**) (50% probability). The H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Ni(1)−C(1), 1.702(2); Ni(1)−P(2), 2.1913(6); Ni(1)−P(1), 2.1949(6); Ni(1)−P(3), 2.1974(6); O(1)−C(1), 1.175(3); C(1)−Ni(1)−P(2), 127.28(8); C(1)−Ni(1)−P(1), 121.37(8); P(2)−Ni(1)−P(1), 93.88(2); C(1)−Ni(1)−P(3), 117.51(8); P(2)−Ni(1)−P(3), 94.58(2); P(1)−Ni(1)−P(3), 94.60(2); C(1)−O(1)−Li(1), 151.1(2); O(1)−C(1)−Ni(1), 175.7(2).

Table 1. CO Stretching Frequencies and Ni−C Bond Distances for $L_3Ni(0)CO$ Complexes

entry	complex	ν_{CO} (cm^{-1})	ref
1	$[\mathrm{Ni(PhBP_3)(CO)}][\mathrm{Li(THF)_3}]$	1812	this work
2	$\mathrm{Ni[N(CH_2CH_2PPh_2)_3](CO)}$	1878	15
3	$\mathrm{Ni[MeC(CH_2PPh_2)_3](CO)}$	1901	16
4	$\mathrm{Ni[PPh(PPh_2CH_2CH_2)_2](CO)}$	1903	this work[17]
5	$\mathrm{Ni(DPB)_2(CO)}$	1910	18
6	$\mathrm{Ni[P(OC_6H_5)_3]_3(CO)}$	1996	19

ing the corresponding isocyanide complexes, encountered by us and Peters.[14] The ^{31}P{^{1}H} NMR spectrum of **1** in THF showed a singlet at 26.7 ppm. The solid state IR spectrum showed an intense ν(CO) stretching band at 1812 cm^{-1}, while the solution IR in THF showed the band shifting to 1869 cm^{-1}. This is typical behavior for the transformation of an alkali metal ion isocarbonyl to a solvent-separated ion pair in solution, where the alkali metal ion becomes associated with solvent THF molecules.[8,10]

The CO stretching frequencies of several nickel(0) monocarbonyl complexes with tridentate phosphine ligands are listed in Table 1 for comparison. Complexes **2**−**6** exhibit the normal inverse correlation of ν(CO) with ligand donor ability. In comparison, complex **1** has an anomalously low ν(CO) value.

Single crystals of **1** were obtained by slow diffusion of diethyl ether into a THF solution of **1**. The crystal structure of **1** (Figure 1) shows the pseudo-tetrahedral nickel center, expected for a nickel(0) complex. The three phosphorus atoms bind to the nickel atom facially, with all three P−Ni−P angles approximately 90°. The Ni−C bond distance is 1.702(2) Å, while the C−O distance is 1.175(3) Å. Table 2 lists selected bond distances of mononuclear Ni(0) carbonyls for comparison.

Table 2. Selected Bond Distances for Mononuclear Ni(0) Carbonyls

complex	Ni−C(O), Å	C−O, Å	ref
$[\mathrm{Ni(PhBP_3)(CO)}][\mathrm{Li(TMED)}]$	1.702(2)	1.175(3)	this work
$\mathrm{Ni[N(CH_2CH_2PPh_2)_3](CO)}$	1.74(2)	1.18(2)	20
$\mathrm{Ni(C_8H_{18}N_4)(CO)_2}$	1.85(6,1)	1.06	21
$\mathrm{Ni[PhPH(CH_2)_3PPhH](CO)_2}$	1.746(9,2)	1.129	22
$\mathrm{Ni(PPh_3)_2(CO)_2}$	1.763(3)	1.142	23
$\mathrm{Ni(CO)_3P(CMe_3)_3}$	1.72(5,4)	1.185	24
$\mathrm{Ni(CO)_4}$	1.817(2)	1.127(3)	25

The most striking feature of the crystal structure is the coordination of the carbonyl oxygen to the lithium cation with a Li−O bond distance of 1.924(5) Å. The coordination geometry around lithium is pseudo-tetrahedral, with the CO and three THF oxygen atoms occupying the apical sites. It should be noted that the Li−O$_{\mathrm{carbonyl}}$ distance is within the range of the distances found between lithium and the oxygen atoms of the THF molecules. As discussed by Darensbourg,[8,10] THF, a ubiquitous solvent used in carbonylate chemistry, is evidently of O atom basicity similar to anions such as $\mathrm{Co(CO)_4^-}$, $\mathrm{Mn(CO)_5^-}$, and $\mathrm{CpFe(CO)^{2-}}$. The isocarbonyl bond angle, C(1)−O(1)−Li(1), is 151.1(2)°. The bent structure in conjunction with the relatively short Ni(1)−C(1) distance, long C(1)−O(1) distance, and similar carbonyl and THF O atom−Li$^+$ bond distances underscore the importance of valence bond structure **A** (Scheme 2), a result of substantial back-donation from the nickel atom to the carbonyl ligand.

Recent research results on the [PhBP$_3$] ligand by Peters et al. showed strong ligand-field donor strength of [PhBP$_3$], suggesting appreciable communication between the anionic phosphine borate ligand and the metal center.[26,27] This appears to result from an electrostatic polarization of the d_π orbitals of the metal by the negatively charged [PhBP$_3$] ligand.

Results of a density functional theory (DFT) electronic structure calculation support this view of electronic charge delocalization to the CO ligand.[28] The structure of the anion of **1**, $[\mathrm{Ni(PhBP_3)(CO)}]^-$, was theoretically determined by performing a geometry optimization based on the crystal structure of **1** as a starting point. The structure calculation converged with reasonable

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(14) In our attempts to prepare Ni(0)[BP3](CNxylyl)[Li(TMED)], we were only able to isolate a mixture of Ni(I) and Ni(0) complexes. The same observations were obtained by the Peters group (Jonas C. Peters, personal communication).

(15) Bianchini, C.; Zanobini, F.; Aime, S.; Gobetto, R.; Psaro, R.; Sordelli, L. *Organometallics* **1993**, *12*, 4757−4763.

(16) Chatt, J.; Hart, F. A. *J. Chem. Soc. Abstr.* **1965**, 812−813.

(17) See Experimental Section.

(18) Corain, B.; De Nardo, L.; Favero, G. *J. Organomet. Chem.* **1977**, *125*, 105−114.

(19) Olechowski, J. R. *J. Organomet. Chem.* **1971**, *32*, 269−271.

(20) Ghilardi, C. A.; Sabatini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 2763−2767.

(21) Hausen, H. D.; Krogmann, K. *Z. Anorg. Allg. Chem.* **1972**, *389*, 247−253.

(22) Baacke, M.; Morton, S.; Stelzer, O.; Sheldrick, W. S. *Chem. Ber.* **1980**, *113*, 1343−1355.

(23) Krueger, C.; Tsay, Y. H. *Cryst. Struct. Commun.* **1974**, *3*, 455−458.

(24) Pickardt, J.; Roesch, L.; Schumann, H. *Z. Anorg. Allg. Chem.* **1976**, *426*, 66−76.

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

(26) Jenkins, D. M.; Di Bilio, A. J.; Allen, M. J.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 15336−15350.

(27) Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2003**, *42*, 5074−5084.

(28) The calculation was performed on Titan1,0,8, with the LACVP* basis set.

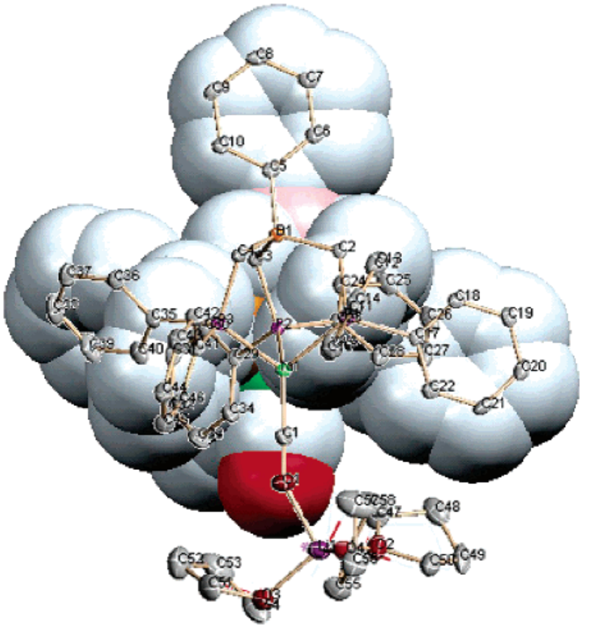

Figure 2. Space-filling representation for complex [Ni(PhBP$_3$)(CO)][Li(THF)$_3$] (**1**).

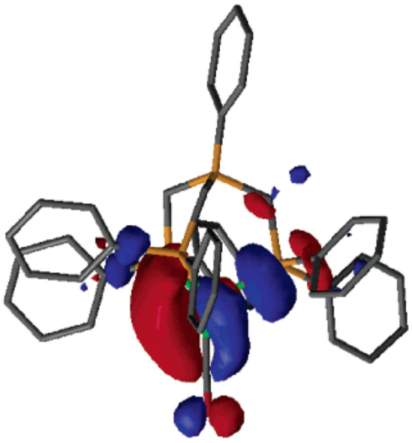

Figure 3. Depiction of the highest occupied molecular orbital (HOMO) of the anion [Ni(PhBP$_3$)(CO)]$^-$ of complex **1** computed in a DFT calculation.

agreement between the theoretical structure of **1** and the crystal structure that was determined experimentally.[29] The calculated atomic charge on the carbonyl oxygen is −0.52. The calculated charge on the nickel atom is +0.75, suggesting significant back-bonding, which corroborates well with the short Ni−C bond distance and low CO stretching frequency determined experimentally. The electronic structure of **1** determined by DFT also suggests that the HOMO orbital is mainly composed of the CO antibonding orbital and the nickel dπ orbitals consisting of d$_{x^2-y^2}$, d$_{xy}$, and d$_{xz}$, which back-bond strongly to the CO π* orbital (Figure 3).

Conclusions

An anionic zerovalent nickel carbonyl complex with a [PhBP$_3$] backbone was synthesized and characterized. The crystal structure shows a lithium cation binding to the carbonyl oxygen atom in an isocarbonyl linkage. A DFT calculation shows significant charge redistribution from the nickel atom to the carbonyl oxygen, consistent with this view. Complex [Ni(PhBP$_3$)(CO)][Li(TMED)] (**1**) represents the first example of Lewis acid O atom complexation to a Ni(0) carbonyl ligand. These results illustrate the powerful electron-donating nature of the [PhBP$_3$] ligand.

Experimental Section

General Methods. Unless noted otherwise, all manipulations were performed under N$_2$ atmosphere either by Schlenk techniques or in an inert atmosphere glovebox. Solvents were HPLC grade and dried over a two-column solid state purification system. Triphos (triphos = bis(2-diphenylphosphinoethyl)-phenylphosphine) was purchased from Strem and was used as received. Ni(COD)$_2$ and [Li(TMED)][PhB(CH$_2$PPh$_2$)$_3$] were prepared by literature methods. ^{1}H and ^{31}P NMR spectra were obtained using a Varian 400 spectrometer. NMR solvents were obtained from Cambridge Isotope Laboratories. ^{1}H chemical shifts were referenced to internal solvent peaks. ^{31}P chemical shifts were referenced with respect to external 85% H$_3$PO$_4$. Solid state FT-IR spectra were collected using a Mattson Research series infrared spectrometer. Crystallography data were collected by a Bruker SMART APEX CCD X-ray diffractometer. Elemental analyses were performed by H. Kolbe Microanalytical Laboratories, Mülheim.

[Ni(PhBP$_3$)(CO)][Li(TMED)] (1). A toluene suspension of Ni(COD)$_2$ (138 mg, 0.5 mmol) was added slowly to the toluene solution (30 mL) of [Li(TMEDA)][BPh(CH$_2$Ph$_2$P)$_3$] (405 mg, 0.5 mmol). CO was then bubbled into the reaction mixture. The color of the solution changed from orange-yellow to yellow. The reaction mixture was allowed to stir for 12 h, and the resulting yellow precipitate was collected by filtration and washed with diethyl ether three times. The product was dried under vacuum to give 195 mg of yellow powder. Yield: 44%.

Solid state IR showed intensive ν(CO) at 1812 cm^{-1}, while solution IR in THF showed intensive ν(CO) at 1869 cm^{-1}. ^{31}P{^{1}H} NMR (THF): δ 26.7 ppm. ^{1}H NMR (d_8-THF) δ 6.8−7.6 (35H, br, C$_6$H$_5$); 1.1 (6H, br, BCH$_2$); 2.3 (4H, s, −CH$_2$− in TMED); 2.2 (12H, s, −CH$_3$ in TMED). ^{13}C NMR (d_8-THF) δ 210.6 (br, C$_{\text{carbonyl}}$). Anal. Calcd for C$_{52}$H$_{57}$BLiN$_2$NiOP$_3$: C, 69.75; H, 6.42; N, 3.13; P, 10.37. Found: C, 69.88; H, 6.37; N, 3.17; P, 10.23.

Vapor diffusion of diethyl ether into the THF solution of complex **1** yielded single crystals suitable for X-ray crystallography.

Ni(triphos)(CO) (4). A toluene suspension of Ni(COD)$_2$ (138 mg, 0.5 mmol) was added slowly to the toluene solution (30 mL) of triphos (267 mg, 0.5 mmol). CO was then bubbled into the reaction mixture. The yellow reaction solution was allowed to stirr for 12 h, and the resulting yellow precipitate was collected by filtration and washed with diethyl ether three times. The product was dried under vacuum to give 165 mg of yellow powder. Yield: 53%.

Solid state IR of complex **4** showed intensive ν(CO) at 1903 cm^{-1}. ^{31}P{^{1}H} NMR (THF): δ 48.9 (d), 64.9 (t). ^{1}H NMR (d_8-THF) δ 7.0−7.9 (25H, br, C$_6$H$_5$); 1.6−2.4 (8H, br, PCH$_2$CH$_2$P). ^{13}C NMR (d_8-THF) δ 206.9 (m, C$_{\text{carbonyl}}$). Anal. Calcd for C$_{35}$H$_{33}$NiOP$_3$: C, 67.73; H, 5.36; P, 14.96. Found: C, 67.61; H, 5.40; P, 14.95.

Acknowledgment. We gratefully acknowledge the DOE (DE-FG03-99ER14992) for support.

Supporting Information Available: Tables of selected bond distances and angles of calculated and experimental results, crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) See Supporting Information: Table 1 Selected bond distances and angles of calculated and experimental results.