

Coordination of a Diphosphine–Ketone Ligand to Ni(0), Ni(I), and Ni(II): Reduction-Induced Coordination

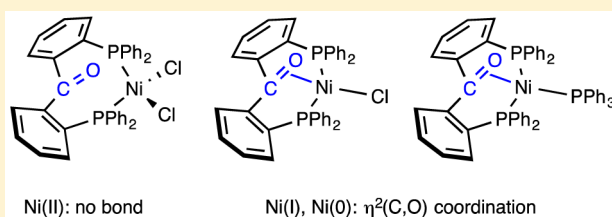
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Supporting Information

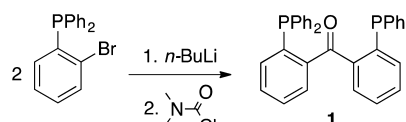
ABSTRACT: The coordination chemistry of the diphosphine–ketone ligand 2,2′-bis(diphenylphosphino)benzophenone (^{Ph}dpbp) with nickel is reported. The ketone moiety does not bind to Ni(II) in the complex (^{Ph}dpbp)NiCl₂, whereas reduction to Ni(I) or Ni(0) induces $\eta^2(\text{C},\text{O})$ coordination of the ketone to form the pseudotetrahedral complexes (^{Ph}dpbp)NiCl and (^{Ph}dpbp)Ni(PPh₃). DFT calculations indicate that the metal–ketone bond is dominated by π back-donation; hence, ^{Ph}dpbp functions as a hemilabile acceptor ligand in this series of complexes.



The development of greener and less expensive chemical processes has motivated a widespread investigation of complexes of first-row transition metals as potential homogeneous catalysts to replace or, better, improve on traditional systems that are widely based on noble metals.¹ Progress in this area has been intimately related to the development of tailored ligands: cooperative ligands² that actively participate in chemical reactions—e.g. by accepting and releasing electrons,³ protons,⁴ or hydride equivalents⁵—and hemilabile ligands⁶ that facilitate reaction steps by adapting their coordination mode to the electronic structure of the metal center along the reaction coordinate. In particular, multidentate ligands containing a Lewis acidic moiety tethered to one or more chelating arms have recently been subjected to intense scrutiny⁷ and were found to facilitate several catalytic reactions such as hydrogenation⁵ (bifunctional H₂ activation) and N₂ reduction⁸ (hemilabile behavior).

Ketones are known to form relatively weak coordination bonds in two distinct modes: $\eta^1(\text{O})$ with electrophilic metals⁹ and $\eta^2(\text{C},\text{O})$ with electron-rich metals.¹⁰ Because of the electronegativity of oxygen, the latter binding mode, described by the Dewar–Chatt–Duncanson model, is often dominated by π back-bonding; for example, the formation of complexes of the type (Et₃P)₂Ni(η^2 -benzophenone) from (Et₃P)₄Ni and substituted benzophenones is strongly accelerated by electron-withdrawing substituents.^{10a} Thus, we reasoned that a ketone moiety tethered to chelating arms would be of interest as a hemilabile, pincer-type ligand featuring a strong π acceptor in the central position.¹¹ The ligand 2,2′-bis(diphenylphosphino)-benzophenone¹² (^{Ph}dpbp (**1**); Scheme 1) has been applied as a coligand for chirality transfer in rhodium¹³ and ruthenium¹⁴

Scheme 1. Synthesis of the ^{Ph}dpbp Ligand



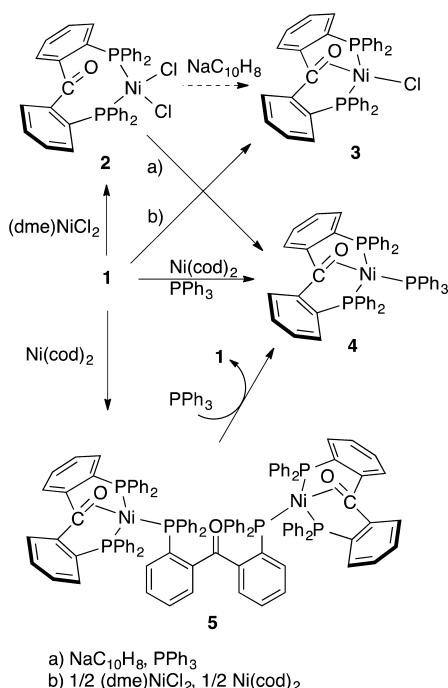
hydrogenation catalysts but to our knowledge has not been used in first-row transition-metal chemistry.

Here we report on the coordination chemistry of the ^{Ph}dpbp ligand to nickel in three different oxidation states, showing that it can act as a wide bite angle bidentate ligand for Ni(II) and adopts a pincer-like geometry in Ni(I) and Ni(0) complexes, in which the ketone moiety is coordinated in an η^2 fashion dominated by π back-donation.

In an improvement on Ding's original five-step synthesis,¹² ligand ^{Ph}dpbp (**1**) was synthesized in 84% yield from *o*-bromo(diphenylphosphino)benzene¹⁵ by lithiation with *n*-BuLi followed by reaction with 0.5 equiv of *N,N*-dimethylchloroformamide (Scheme 1). Reaction of **1** with (dme)NiCl₂ (dme = 1,2-dimethoxyethane) in dichloromethane afforded 83% of the 1:1 complex **2** as brown crystals (Scheme 2). Broad ¹H NMR resonances ranging from −6.6 to 20.7 ppm and a solution effective magnetic moment (μ_{eff}) of 2.8 μ_{B} indicate a paramagnetic *S* = 1 state consistent with a high-spin Ni(II) center. Complex **2** displays an intense IR band at 1634 cm^{−1}, only slightly shifted from the C=O band in the free ligand **1** (1661 cm^{−1}), suggesting at most a weak interaction of the C=O moiety with the metal.

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Scheme 2. Coordination of the ^{ph}dpbp Ligand to Ni(0), Ni(I), and Ni(II)



Crystallization of **2** from CH₂Cl₂ resulted in two crystal forms, which were both analyzed by X-ray crystal structure determinations. The results for the solvent-free **2** are discussed here (Figure 1). For the results of **2**·CH₂Cl₂, see the Supporting Information. The Ni–C (3.4031(12) Å) and Ni–O (3.1012(10) Å) distances are large enough to exclude coordination of the carbonyl moiety but are nevertheless shorter than the sum of van der Waals radii¹⁶ (Ni–C = 4.17 Å; Ni–O = 3.90 Å), which is likely imposed by the rigidity of the *o*-phenylene linkers but may result in a weak interaction. Hence, the coordination geometry is best described as distorted tetrahedral with a P–Ni–P bite angle of 112.996(13)° and a large Cl–Ni–Cl angle (133.302(14)°). Similar distortions have been observed in NiCl₂ complexes of other diphosphine ligands with large bite angles and ascribed to lone-pair repulsion between Cl atoms.^{17a}

The nickel(I) complex **3** was accessed via comproportionation of (dme)NiCl₂ and Ni(cod)₂ in the presence of ligand **1** (Scheme 2). Complex **3** was also observed by NMR following direct reduction of **2** with sodium naphthalide but could not be

isolated from the reaction mixture (see the Supporting Information). Its crystal structure¹⁸ (Figure 1) reveals a mononuclear, four-coordinate complex in which the ketone unit is coordinated to the nickel in an η² fashion (Ni–C = 2.006(2) Å, Ni–O = 1.9740(15) Å). Significant π back-donation into the C=O fragment is evidenced by an elongated C=O bond (1.310(2) Å vs 1.213(3) Å in **1**¹²) and the pyramidalization of the C71 atom, which displays a sum of valence angles of 354.1(3)°. The overall coordination geometry is best described as slightly distorted tetrahedron, in line with known tris(phosphine)Ni^I–X (X = I, Br, Cl) complexes.¹⁹ To our knowledge, **3** is the first example of a structurally characterized η²(C,O)-ketone complex of Ni(I). The η¹(O) binding mode is known in the Ni(I) complex [(Nacnac)Ni(O=CPh₂)] (Nacnac = HC[CMcNC₆H₃(*i*-Pr)₂]₂),²⁰ which displays a much shorter C–O distance (1.239(7) Å), indicating a lower extent of π back-donation than in **3**. The preference for the η²(C,O) mode in **3** can be attributed to (i) a more electron rich Ni(I) center and (ii) geometrical constraints imposed by the rigid *o*-phenylene linkers.

Samples of **3**—even after multiple recrystallizations—contain a diamagnetic component evidenced by aromatic ¹H NMR resonances between 6.5 and 8 ppm (next to the expected broad, paramagnetically shifted spectrum) and a single ³¹P resonance at 30.6 ppm, which we tentatively attribute to a Ni–Ni bonded species.^{21,22} The IR spectrum of **3** displays no absorption corresponding to an unbound ketone but exhibits two absorptions at 1331 and 1340 cm^{−1} that do not appear in the spectrum of the free ligand and are assigned to the bound C=O moiety (see the Supporting Information). More insight into the electronic structure of compound **3** was obtained by EPR spectroscopy and DFT calculations.²³ The room-temperature EPR spectrum of **3** (Figure 2) displays a broad doublet

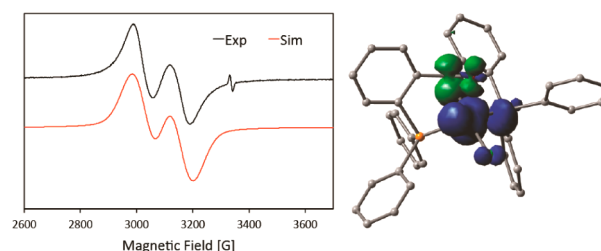


Figure 2. (left) Experimental (black) and simulated (red) room-temperature X-band EPR spectra of **3**. Simulation parameters: *g* = 2.177, *A*_{iso}(³¹P) = 380 Hz. (right) Spin density of **3** calculated at the B3LYP/6-31G(d,p) level.

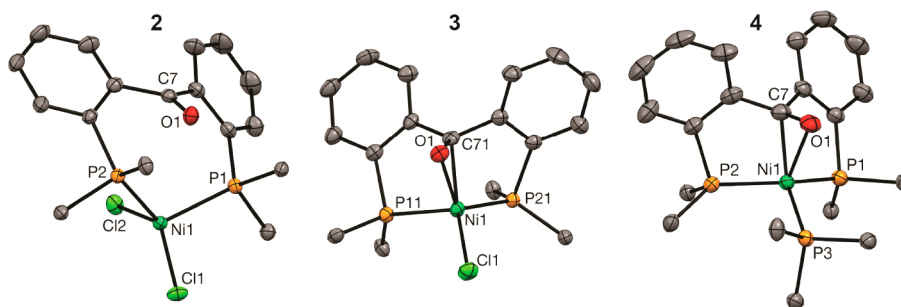


Figure 1. Molecular structures of compounds **2**–**4** in the crystal (50% probability level), determined by single-crystal X-ray structure determination. For clarity, only the ipso C atoms of phosphorus-bound phenyl groups are represented. Only one of the two independent molecules of **3** is represented, and an Et₂O molecule in the solid-state structure of **4** is omitted.

($A_{\text{iso}}(^{31}\text{P}) = 380 \text{ MHz}$) centered at $g = 2.177$, consistent with a metal-centered radical with superhyperfine coupling to one of the ^{31}P nuclei. A spectrum recorded at 100 K in frozen toluene (Figure S25 in the Supporting Information) displays a complex pattern that can be adequately simulated as a rhombic signal ($g_x = 2.325$, $g_y = 2.175$, $g_z = 2.026$) with anisotropic hyperfine coupling to two inequivalent ^{31}P nuclei ($A_1(^{31}\text{P}) = [360, 300, 500] \text{ MHz}$, $A_2(^{31}\text{P}) = [210, 100, 95] \text{ MHz}$). The spin density obtained from DFT at the B3LYP/6-31G(d,p) level (Figure 2) suggests that the inequivalency of the two ^{31}P nuclei both at 100 K and at room temperature—where only one hyperfine coupling is resolved—can be ascribed to delocalization of the unpaired electron on a single P atom: NBO^{24,25} analysis of the spin density ascribes a natural spin density (NSD) of 1.026 to Ni and of respectively 0.094 and 0.004 to the two phosphorus atoms, supporting the predominant metalloradical character of **3**. Negative NSDs on the ketone C (−0.12) and O (−0.04) atoms suggest that a charge-transfer configuration (Ni(II) + ketyl radical anion) might contribute to the overall electronic structure of **3**.

To study its coordination to Ni(0) centers, ligand **1** was treated with 1 equiv of Ni(cod)₂ to afford a brown solid that is formulated as the ligand/metal 3/2 complex **5** (Scheme 2) on the basis of NMR data. The ^{31}P NMR spectrum of **5** at room temperature consists of three broad peaks that sharpen upon heating to 100 °C, becoming three mutually coupled doublets of doublets at 44.4, 21.3, and 5.6 ppm (Figure S20 in the Supporting Information). The ^1H NMR spectrum of **5** exhibits a complex set of aromatic signals ranging from 8.8 to 6.2 ppm and no additional signal that would suggest the presence of other organic ligands. The simplest structure that is consistent with this data is a symmetrical dinuclear complex in which a central ^{Ph}dppb ligand bridges two Ni(0) centers chelated by an additional ^{Ph}dppb ligand each (Scheme 2). This structural model is further corroborated by bands at 1679 and 1310 cm^{−1} in the IR spectrum of **5** corresponding to the unbound and bound C=O units, respectively.

When a solution of **5** in toluene-*d*₇ was treated with excess PPh₃ in an NMR tube, 2 equiv of the mononuclear complex **4** formed with concomitant release of 1 equiv of the free ligand **1** (Scheme 2). Complex **4** could also be synthesized as a brown solid from the reaction of **1**, Ni(cod)₂, and PPh₃ or by direct reduction of **2** with 2.2 equiv of sodium naphthalide in the presence of PPh₃. Its ^{31}P NMR spectrum consists of a triplet at 38.2 ppm ($^2J_{\text{P,P}} = 25 \text{ Hz}$) and a doublet at 17.9 ppm in a 1/2 integral ratio, indicating that the two ^{31}P nuclei from the ^{Ph}dppb ligand are equivalent on the ^1H NMR time scale, in contrast with compound **5**. This can be explained by the less sterically congested structure of **4**, which allows for rapid exchange of the P atoms (see the Supporting Information for an extended discussion). The η^2 -coordinated ketone is characterized by a doublet ($^2J_{\text{P,C}} = 14 \text{ Hz}$) of triplets ($^2J_{\text{P,C}} = 9 \text{ Hz}$) at 120.4 ppm in the ^{13}C NMR spectrum and an IR absorption at 1309 cm^{−1}.

The X-ray crystal structure of **4** (Figure 1) reveals a pseudotetrahedral environment of the metal similar to that found in **3**, albeit with a significantly larger P–Ni–P angle (120.65(2)° vs 107.57(2)°). The C=O bond (1.330(3) Å) is somewhat more elongated than that in **3**, consistent with stronger π back-donation from Ni(0). The Ni–C (2.001(2) Å) and Ni–O (2.0091(14) Å) distances are longer than those in three-coordinate (R₃P)₂Ni(benzophenone) complexes (Ni–C

= 1.97–1.99 Å; Ni–O = 1.84–1.87 Å),¹⁰ which might be due to more steric congestion.

More insight into the bonding of the carbonyl fragment to Ni was obtained from NBO^{24,25} analysis performed on ligand **1** and complexes **2**–**4** (Table 1). Coordination of the ^{Ph}dppb

Table 1. Wiberg Bond Indices (WBI) and Natural Charges (*q*) from Densities Calculated at the B3LYP/6-31+G(d,p) Level

	1	2	3	4
WBI(C–O)	1.75	1.67	1.30	1.23
WBI(Ni–O)		<0.01	0.33	0.30
WBI(Ni–C)		<0.01	0.46	0.50
<i>q</i> (C)	0.58	0.56	0.18	0.12
<i>q</i> (O)	−0.54	−0.55	−0.69	−0.73
<i>q</i> (C) + <i>q</i> (O)	0.04	0.01	−0.51	−0.61

ligands through its P atoms in **2** induces a slight decrease of the C–O Wiberg bond index (WBI), consistent with the observed shift of the corresponding IR band from 1661 to 1634 cm^{−1}; however, the orbital interaction between the Ni center and the C=O moiety is minimal, with Ni–C and Ni–O WBIs below 0.01. In contrast, the C–O WBI decreases upon binding from 1.75 in the free ligand **1** to 1.30 in **3** and 1.23 in **4**. Interestingly, the Ni–O WBIs in **3** (0.33) and **4** (0.30) are lower than the corresponding Ni–C WBIs (0.46 in **3**, 0.50 in **4**), suggesting that back-donation into the $\pi^*(\text{C}=\text{O})$ orbital (which has a larger coefficient on C) contributes more to the bonding than donation from the $\pi(\text{C}=\text{O})$ orbital. The primarily acceptor character of the C=O moiety is additionally corroborated by a decrease of the total charge of the C–O fragment by 0.55 and 0.65 e upon coordination to Ni(I) in **3** and to Ni(0) in **4**, respectively. In accordance, NBO analysis performed on the Ni(0) complex **4** characterizes the (Ni–C–O) triangle as engaging in three-center–four-electron bonding (Figures S29 and S30 in the Supporting Information).

In summary, we have studied the coordination chemistry of the *o*-phenylene-bridged diphosphine–ketone (^{Ph}dppb) ligand **1** with nickel, showing that the central ketone moiety in **1** can act as a hemilabile moiety. In the Ni(II) complex **2**, the ^{Ph}dppb ligand acts as a flexible, wide bite angle diphosphine ligand¹⁷ and the ketone moiety is not bound to the metal. Moving to more reduced Ni(I) and Ni(0) complexes induces coordination of the ketone so that the ^{Ph}dppb ligand acts as a tridentate, pincer-like ligand. Consequences of this acceptor-hemilabile behavior in small-molecule activation and catalysis are currently under investigation in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF and XYZ files giving experimental and computational details, characterization data for all compounds, crystallographic data, and DFT-optimized coordinates. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00264.

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Notes

The authors declare no competing financial interest.

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