Synthesis and Reactions of $[Co(RCN)\{PPh(OEt)_2\}_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ Derivatives: Strong Evidence for η^2-Coordination of the Phenyl Ring of the $C_6H_5PO(OEt)_2$ Ligand

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Summary: Cobalt(I) complexes $[Co(RCN)P_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (**1**; *R* = *Me, Ph; P* = $PPh(OEt)_2$) *were prepared by allowing* $[CoClP_4]BPh_4$ *compound to react with zinc dust in a cosolvent mixture of nitrile and ethanol.* η^2*-Coordination of the arene ring of the* $C_6H_5PO(OEt)_2$ *ligand was confirmed by* ^1H *and* ^{13}C *NMR spectra and decoupling experiments. Substitution reactions with CO or isocyanide gave free* $C_6H_5PO(OEt)_2$*, RCN, and* $[Co(CO)_2P_3]^+$ *or* $[Co(RNC)_2P_3]^+$ *cations. Treatment of* **1** *with* H_2 *(1 atm), in either the presence or absence of a heterogeneous catalyst, gave the unstable cobalt(III) dihydride derivative* $[CoH_2P_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]^+$.

The coordination of aromatic molecules to transition metals in an η^2-fashion is rather uncommon,[1] although these complexes are suspected to be intermediates in C−H activation and other catalytic processes.[1,2] Recent papers[3] have in fact shown how η^2-coordination activates the arene molecule toward selective hydrogenation to alkene. The involvement of η^2-species in C−H activation of aromatic molecules has also been the subject of some studies.[1c,2a]

We now report a new example of η^2-coordination of an arene molecule involving the phenyl ring of the $C_6H_5PO(OEt)_2$ ligand, bound to a cobalt[4] central atom in an η^2-fashion.

Scheme 1[a]

$$[CoClP_4]^+ \xrightarrow[\text{RCN, EtOH}]{\text{Zn dust}} [Co(RCN)P_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]^+$$

1

[a] Legend: P = $PPh(OEt)_2$; R = Me (**a**), Ph (**b**).

Treatment of the complex[5] $[CoCl\{PPh(OEt)_2\}_4]BPh_4$ in an ethanol−nitrile (MeCN or PhCN) solution with zinc dust gives a dark red solution from which, after workup, a red solid[6] characterized[7] as $[Co(RCN)\{PPh(OEt)_2\}_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (**1**) was obtained in about 45% yield[8] (Scheme 1).

The IR spectra show one weak band at 2278 cm^{-1} (**1a**) and one at 2239 cm^{-1} (**1b**), due to the coordinated nitrile, and a strong band at 1240 cm^{-1} attributed to the $\nu_{P=O}$ of the $C_6H_5PO(OEt)_2$ ligand. At room temperature, the $^{31}P\{^1H\}$ NMR spectra of **1** in CD_2Cl_2 display

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[1] (a) Muetterties, E. L.; Blecke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (b) Sweet, J. R.; Graham, A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305; *Organometallics* **1983**, *2*, 135. (c) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (d) van der Heijden, H.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576. (e) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883. (f) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725. (g) Chordia, M. D.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 5637.

[2] (a) Parshall, G. W.; Ittel, S. D. In *Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; Wiley: New York, 1992. (b) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843.

[3] (a) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7906. (b) Harman, W. D.; Schaefer, W. P.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682. (c) Chin, R. M.; Dong, L.; Duckett, S. B.; Jones, W. D. *Organometallics* **1992**, *11*, 871. (d) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.

[4] For our previous papers on cobalt(I) complexes, see: (a) Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Pelizzi, G. *Organometallics* **1995**, *14*, 4126. (b) Albertin, G.; Antoniutti, S.; Bordignon, E. *Organometallics* **1990**, *9*, 2177. (c) Albertin, G.; Amendola, P.; Antoniutti, S.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1990**, 2979. (d) Albertin, G.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1986**, 2551.

[5] Bertacco, A.; Mazzi, U.; Orio, A. A. *Inorg. Chem.* **1972**, *11*, 2547.

[6] All synthetic work was carried out under an inert atmosphere using Schlenk techniques; solvents used were degassed and purified by standard methods. Compounds **1** were prepared as follows. In a 50-mL three-necked round-bottomed flask 4 g (3.3 mmol) of $[CoCl(PPh(OEt)_2)_4]BPh_4$[5] was dissolved in a cosolvent mixture of 10 mL of ethanol and 15 mL of acetonitrile for **1a** or in benzonitrile for **1b**, and the solution was treated at room temperature with an excess of zinc dust (15 mmol, 1 g). The reaction mixture was stirred for 2 h, filtered through silica gel, and then evaporated to dryness under reduced pressure. During evaporation, the temperature of the solution must be kept below 30 °C. The resulting oil was dissolved in ethanol (8 mL) and treated with an excess of $NaBPh_4$ (10 mmol, 3.4 g) dissolved in 5 mL of ethanol. A red solid separated out, which was filtered and crystallized from CH_2Cl_2 (5 mL) and ethanol (15 mL); yield 45%. Note that, to avoid the formation of oil, crystallization should be carried out at 0 °C using ethanol containing a small amount of MeCN or PhCN as precipitating agent. Furthermore, compounds **1** are air-sensitive and must be handled under an inert atmosphere.

[7] The NMR spectra were recorded on a Bruker AC200 instrument. ^1H and ^{13}C NMR chemical shifts are referenced to internal $SiMe_4$, ^{31}P shifts are referenced to 85% H_3PO_4 with downfield shifts considered positive. Anal. Calcd for $C_{66}H_{83}NBO_9P_4Co$ (**1a**): C, 64.55; H, 6.81; N, 1.14. Found: C, 64.40; H, 6.73; N, 1.10. Λ_M (CH_3NO_2, 25 °C): 53.6 $\Omega^{-1}\ mol^{-1}\ cm^2$. IR (KBr): 2278 w ν_{CN} cm^{-1}; 1240 s $\nu_{P=O}$ cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.75−6.60 (m, 38H, Ph), 5.63 (d, 1H, H_a), 5.01 (m, 1H, H_b), 4.01, 3.64, 3.39 (m, 16H, CH_2), 1.25, 1.13, 1.04 (t, 24H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): spin system AB_2, δ_A 173.2, δ_B 158.4, J_{AB} = 98 Hz ($PPh(OEt)_2$), 19.58 (s, 1P, $C_6H_5PO(OEt)_2$). ^{13}C NMR (CD_2Cl_2 at 25 °C): δ 165−120 (m, Ph), 97.8 (d of d, C_a, $^1J_{CH}$ = 170 Hz, $^2J_{CP}$ = 10 Hz), 91.3 (d, C_b, $^1J_{CH}$ = 170 Hz), 62.7, 62.2 (m, CH_2), 15.9 (m, CH_3). ^{13}C NMR (CD_3CN at 25 °C): δ 165−120 (m, Ph), 98.3 (d of d, C_a, $^1J_{CH}$ = 170 Hz, $^2J_{CP}$ = 10 Hz), 91.8 (d, C_b, $^1J_{CH}$ = 170 Hz), 65 (m, br, CH_2), 16.5, 16.1 (q, CH_3). Anal. Calcd for $C_{71}H_{85}NBO_9P_4Co$ (**1b**): C, 66.10; H, 6.64; N, 1.09. Found: C, 65.91; H, 6.60; N, 1.08. Λ_M (CH_3NO_2, 25 °C): 54.2 $\Omega^{-1}\ mol^{-1}\ cm^2$. IR (KBr): 2239 w ν_{CN} cm^{-1}; 1240 s $\nu_{P=O}$ cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 8.00−6.60 (m, 43H, Ph), 5.65 (d, 1H, H_a), 5.02 (m, 1H, H_b), 3.70 (m, 16H, CH_2), 1.14 (m, 24H, CH_3). ^1H NMR (CD_3CN, 25 °C): δ 7.85−6.80 (m, 43H, Ph), 5.60 (d, 1H, H_a), 5.17 (m, 1H, H_b), 4.00−3.50 (m, 16H, CH_2), 1.37, 1.10 (t, 24H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ 170, 158 (br, 3P, $PPh(OEt)_2$), 19.64 (s, 1P, $C_6H_5PO(OEt)_2$). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 165−122 (m, Ph), 98.0 (d of d, C_a, $^1J_{CH}$ = 170, $^1J_{CP}$ = 10 Hz), 91.5 (d, C_b, $^1J_{CH}$ = 170 Hz), 62.7 (m, CH_2), 16.4, 16.1 (q, CH_3). ^{13}C NMR (CD_3CN, 25 °C): δ 160−120 (m, Ph), 98.7 (d of d, C_a, $^1J_{CH}$ = 170, $^1J_{CP}$ = 10 Hz), 92.0 (d, C_b, $^1J_{CH}$ = 170 Hz), 63.3 (m, CH_2), 16.6 (m, CH_3).

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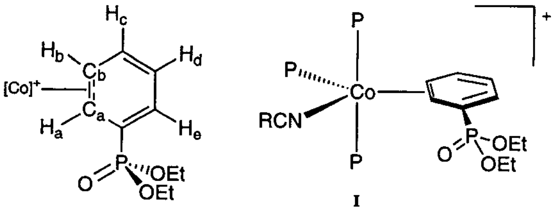
Chart 1



I

a broad signal in the phosphite region near 160 ppm and sharp singlets at 18.9 (**1a**) and 19.4 ppm (**1b**) attributed to the phosphorus *nucleus* of the phenylphosphonic acid diethyl ester ligand $C_6H_5PO(OEt)_2$. Support for this assignment came from the spectra of free[10] $C_6H_5PO(OEt)_2$ liberated from **1** by substitution with CO or isocyanides (see below), and this also confirms the presence of $C_6H_5PO(OEt)_2$ in the complexes. Lowering the sample temperature to −80 °C showed that the singlet at 19 ppm remains unchanged, while the phosphite signal at 160 ppm resolves into an AB_2 multiplet (one triplet and one doublet), suggesting the presence of two phosphites, magnetically equivalent and different from the third. The spectra also show that these phosphorus *nuclei* at 170−160 ppm are not coupled with that at 19 ppm attributed to the $C_6H_5PO(OEt)_2$ ligand. Apart from the signals due to phosphites, nitrile, and BPh_4^-, the ^1H NMR spectra of **1** show two resonances at 5.63 and 5.01 ppm (in CD_2Cl_2) for **1a** and at 5.60 and 5.17 ppm (in CD_3CN) for **1b**, which are attributed to H_a and H_b (Chart 1) of the η^2-bound phenyl ring of the $C_6H_5PO(OEt)_2$ ligand. Support for this attribution comes from integration, a COSY spectrum,[11] and homodecoupling experiments and from a comparison of our spectra with those of previously reported η^2-coordinated arene complexes,[1e,f] which indicate that η^2-complexation shifts the ring protons in proximity to the metal (H_a, H_b) upfield by about 2 ppm from the free ligand resonance, in agreement with our observations.

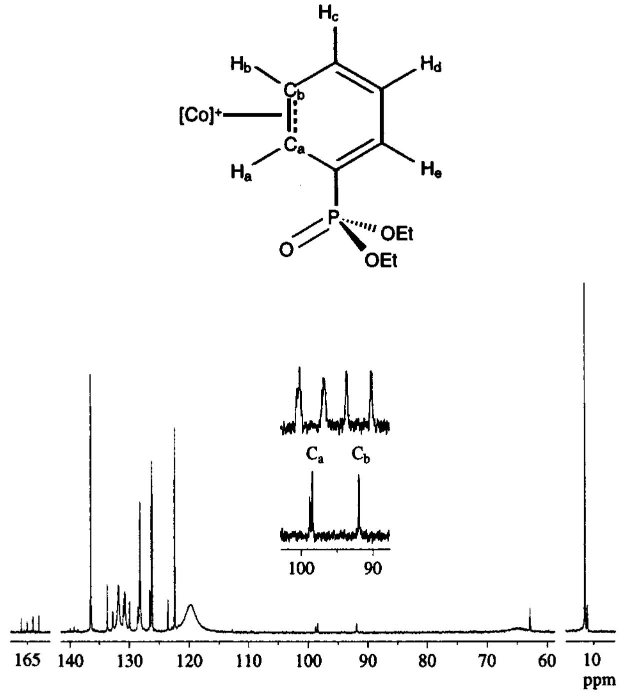


Figure 1. ^{13}C NMR spectra of **1b** in CD_3CN at 25 °C: (bottom) proton-decoupled; (top) proton-coupled.

Lowering the temperature[12] does not change the profile of the spectra, except for a slight signal shift. At −80 °C, however, a new resonance appears near 6.40 ppm for **1b**, which may be attributed to another proton such as H_c, H_d, or H_e, whereas the signals of the other two are probably masked by phosphite or BPh_4 phenyl resonances.

The ^1H NMR spectra also indicate that two $PPh(OEt)_2$ phosphite ligands are in mutually trans positions, showing a complicated multiplet in the methylene region. We therefore tentatively propose a geometry of type **I** (Chart 1) for our cobalt(I) complexes **1a** and **1b**. Further support for this geometry, containing an η^2-coordination of an arene ring, comes from the proton-coupled and -decoupled ^{13}C NMR spectra shown in Figure 1. Two resonances at 98.3 (d) and 91.8 (s) ppm for **1a** and at 98.7 (d) and 92.0 (s) ppm for **1b** appear in the $^{13}C\{^1H\}$ spectra (in CD_3CN), which are split, in the proton-coupled ^{13}C spectra, into a doublet of doublets, the former at 98 ppm, and into a doublet, the latter with a $^1J_{^{13}CH}$ value of 170 Hz. These CH resonances can reasonably be attributed to the C_a and C_b carbon atoms, respectively, of the η^2-coordinated $C_6H_5PO(OEt)_2$ ligand, in agreement with the proposed formulation.

The nitrile ligand in **1** is labile and can be substituted by several ligands such as $PPh(OEt)_2$ and *p*-tolylNC, giving the new $[Co\{PPh(OEt)_2\}_4\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (**2**) and $[Co(p\text{-tolylNC})\{PPh(OEt)_2\}_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (**3**) derivatives (Scheme 2), which can be

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[8] The yields in **1** were always rather low, about 40−45%, and any attempt to isolate other cobalt complexes from the reaction mixture failed. The formation of phenylphosphonic acid diethyl ester, $C_6H_5PO(OEt)_2$, from treatment of the cobalt(II) complex $[CoClP_4]BPh_4$ with a reducing agent such as zinc dust is quite surprising and may be explained by assuming that the reducing agent of Co(II) species to Co(I) is not zinc but the phosphite $PPh(OEt)_2$, affording $C_6H_5PO(OEt)_2$, which then coordinates in an η^2 fashion to the metal, giving **1** as the final product. The role of zinc dust is probably therefore only that of catalyzing the reaction. The reducing properties of phosphite in ethanol to give “phosphite oxide” are known,[9] and this partly supports the proposed path for the reaction.

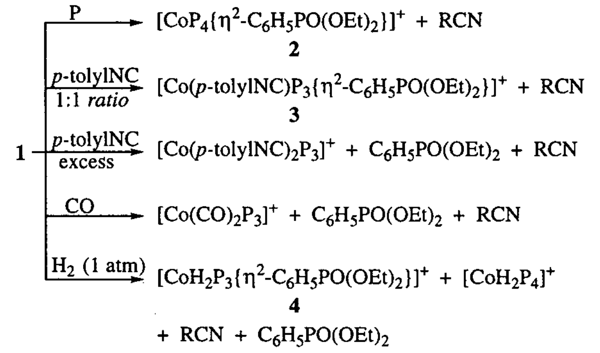
[9] Meier, M.; Basolo, F. *Inorg. Synth.* **1972**, *13*, 112.

[10] The $C_6H_5PO(OEt)_2$ species can be obtained as a colorless oily liquid by reacting **1** with CO or isocyanide, as follows: 117 μL (1 mmol) of *p*-tolylNC is added to a solution of $[Co(PhCN)\{PPh(OEt)_2\}_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (**1b**; 0.5 mmol, 0.65 g) in 10 mL of CH_2Cl_2, and the reaction mixture is stirred for about 4 h. The solvent is removed under reduced pressure, leaving an oil which is triturated with ethanol (10 mL) containing an excess of $NaBPh_4$ (1.2 mmol, 0.41 g). The $[Co(p\text{-tolylNC})_2\{PPh(OEt)_2\}_3]BPh_4$ complex slowly separates out as a yellow solid which is separated by filtration. The remaining solution is evaporated to dryness, giving a pale yellow solid from which the $C_6H_5PO(OEt)_2$ species is extracted with five 5 mL portions of a benzene/petroleum ether (40−60 °C) mixture (1:1). The resulting solution is concentrated to 5 mL and chromatographed through a silica gel column (70 × 2 cm) using acetone as eluent. The first eluate (50 mL) is evaporated to dryness, leaving the phenylphosphonic acid diethyl ester as a colorless oily liquid. The formulation of the compound can be confirmed by GCMS, IR, and ^1H and ^{31}P NMR and by comparison with a sample obtained by oxidation with H_2O_2 of the phosphite $PPh(OEt)_2$. IR (KBr): 1237 s $\nu_{P=O}$ cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.80, 7.10 (br, 5H, Ph), 3.89 (m, br, 4H, CH_2), 1.02 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C): δ 20.97 (s).

[11] As suggested by one reviewer, we obtained a COSY spectrum with a high-field NMR instrument (400 MHz) and observed that the two methyne groups H_a and H_b are correlated to the other ring protons: this further proves the assigned structure.

[12] The presence of two well-resolved resonances at 5−7 ppm at room temperature indicates that the $C_6H_5PO(OEt)_2$ molecule does not tautomerize (for example 2,3-$\eta^2 \rightleftharpoons$ 3,4-η^2) on the time scale of NMR measurements. Increasing the sample temperature caused some decomposition of the complex, with broadening of all proton signals in the spectra: this precludes any information on tautomerization.

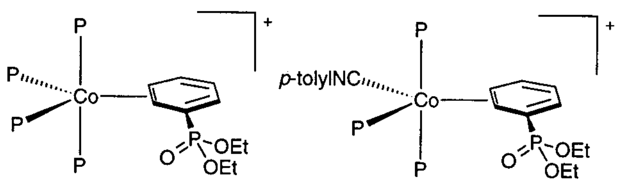
Scheme 2[a]



[a] Legend: P = PPh(OEt)$_2$; R = Me (**a**), Ph (**b**).

isolated as red solids and characterized.[13] Geometries **II** and **III** (Chart 2) for **2** and **3** can also be proposed in solution.

Chart 2



II **III**

The η^2-bound $C_6H_5PO(OEt)_2$ ligand can also be substituted in **1**, affording the free molecule and known[4c,14] cobalt(I) cations $[Co(p\text{-tolylNC})_2P_3]^+$ and $[Co(CO)_2P_3]^+$, as shown in Scheme 2.

Complexes **1** quickly react with H_2 (1 atm) at room temperature to give a colorless solution from which a white solid was isolated.[15] Spectroscopic investigations indicated the presence of two species, one identified as the known[4c] dihydride $[CoH_2\{PPh(OEt)_2\}_4]BPh_4$, and a new hydride, formulated as the $[CoH_2\{PPh(OEt)_2\}_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (**4**) derivative.[15] The IR spectra show a medium-intensity band at 1985 cm^{-1} attributed to ν_{Co-H} and a strong band at 1240 cm^{-1} due to $\nu_{P=O}$ of the $C_6H_5PO(OEt)_2$ ligand. The presence of the η^2-bound phosphate ligand is confirmed by the two CH resonances of the phenyl ring between 5 and 6 ppm in the ^1H NMR spectra and by the singlet at 19.7 ppm observed in the phosphorus spectra. A broad signal at low frequency (near −8 ppm), which does not resolve even at −90 °C, is also observed in the proton spectra, in agreement with the presence of the hydride ligands. Although the complex cannot be isolated in the pure form, the IR and NMR data support[16] the proposed formulation for **4**, which appears to be the product of a quite rare example of oxidative addition of H_2 to a cobalt(I) complex,[17] giving a dihydride cobalt(III) derivative.

We also treated **1** with hydrogen in the presence of Pd^0 on carbon (5% Pd/C) in THF at 25 °C, in an attempt to hydrogenate the phenyl ring of the $C_6H_5PO(OEt)_2$ ligand. The results show that the reaction proceeds as in the absence of Pd/C, giving **4** and $[CoH_2P_4]^+$ as the main products, and investigation of the reaction mixture did not show any evidence of a hydrogenation reaction with formation[3a] of the $C_6H_9PO(OEt)_2$ species.

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Supporting Information Available: ^1H NMR and homonuclear decoupling spectra of **1b** (Figure S1) and a COSY spectrum of **1a** (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] The complexes $[CoP_4\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (**2**) and $[Co(p\text{-tolylNC})P_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (**3**; P = PPh(OEt)$_2$) were prepared by reacting **1** with an excess of phosphite or an equimolar amount of isocyanide, as follows. For compound **2**, an excess of PPh(OEt)$_2$ (3 mmol, 0.6 mL) was added to a solution of $[Co(PhCN)P_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (1 mmol, 1.3 g) in 20 mL of CH_2Cl_2 cooled to about −80 °C. The reaction mixture was brought to room temperature and stirred for about 5 h. The solvent was removed under reduced pressure, giving an oil which was triturated with 10 mL of ethanol until a solid separated out, which was filtered and crystallized from CH_2Cl_2 (3 mL) and ethanol (10 mL); yield 90%. Anal. Calcd for $C_{74}H_{95}BO_{11}P_5Co$: C, 64.17; H, 6.91. Found: C, 64.39; H, 6.87. Λ_M (CH_3NO_2, 25 °C): 51.3 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1237 s $\nu_{P=O}$ cm^{-1}. ^1H NMR ($(CD_3)_2CO$, −70 °C): δ 8.20−6.60 (m, 43H, Ph), 5.67 (br, 1H, H$_a$), 5.33 (br, 1H, H$_b$), 4.07, 3.80 (br, 20H, CH$_2$), 1.33, 1.12 (t, 30H, CH$_3$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −70 °C): δ 168.0 (br, 2P, PPh(OEt)$_2$), 160.5 (br, 2P, PPh(OEt)$_2$), 21.6 (s, br, 1P, $C_6H_5PO(OEt)_2$). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C): δ 165−120 (m, Ph), 97.7 (d, C$_a$, $^2J_{CP}$ = 10 Hz), 90.8 (s, C$_b$), 66.3, 61.6 (s, br, CH$_2$), 16.7, 15.0 (s, CH$_3$). For compound **3**, an equimolar amount of *p*-tolylNC (1 mmol, 117 μL) was added to a solution of $[Co(PhCN)P_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (1 mmol, 1.3 g) in 20 mL of CH_2Cl_2 and the reaction mixture stirred for 4 h. The solvent was removed under reduced pressure, giving an oil that was triturated with 5 mL of ethanol until a solid separated out, which was filtered and crystallized from CH_2Cl_2 (3 mL) and ethanol (10 mL); yield 90%. Anal. Calcd for $C_{72}H_{87}NBO_9P_4Co$: C, 66.31; H, 6.72; N, 1.07. Found: C, 66.10; H, 6.70; N, 0.95. Λ_M (CH_3NO_2, 25 °C): 54.7 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2111 s ν_{NC} cm^{-1}; 1236 s $\nu_{P=O}$ cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.70−6.60 (m, 42H, Ph), 5.75 (br, 1H, H$_a$), 5.50 (br, 1H, H$_b$), 4.00, 3.79 (m, 16H, CH$_2$), 2.27 (s, 3H, CH$_3$ isocyanide), 1.23, 1.20 (t, 24H, CH$_3$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −80 °C): δ 164.5 (br, PPh(OEt)$_2$), 19.5 (s, $C_6H_5PO(OEt)_2$).

[14] (a) Albertin, G.; Bordignon, E.; Orio, A. A.; Rizzardi, G. *Inorg. Chem.* **1975**, *14*, 944. (b) Graziani, R.; Albertin, G.; Forsellini, E.; Orio, A. A. *Inorg. Chem.* **1976**, *15*, 2422.

[15] A solution of the complex $[Co(PhCN)\{PPh(OEt)_2\}_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (0.65 mmol, 0.84 g) in 10 mL of CH_2Cl_2 was allowed to stand under an H_2 atmosphere (1 atm) for 3 h, and the solvent was then removed under reduced pressure. The resulting oil was treated with 5 mL of ethanol containing an excess of $NaBPh_4$ (1.3 mmol, 0.4 g) and the solution stirred until a white solid separated out, which was filtered and dried under vacuum. The solid obtained contained a mixture of two products, which could not be separated, either by chromatography or fractional crystallization, owing to the instability of one of the two compounds. However, IR and NMR data identified the known dihydride $[CoH_2\{PPh(OEt)_2\}_4]BPh_4$[4c] in the mixture, besides the new species characterized as $[CoH_2\{PPh(OEt)_2\}_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]BPh_4$ (**4**). Its spectroscopic data are as follows. IR (Nujol): 1985 m ν_{Co-H} cm^{-1}; 1240 s $\nu_{P=O}$ cm^{-1}. ^1H NMR ($(CD_3)_2CO$ at −90 °C): δ 7.80−6.70 (m, Ph), 4.80 (br, H$_a$), 4.51 (br, H$_b$), 3.52 (m, CH$_2$), 1.08 (br, CH$_3$), −8.75 (m, br, hydride). ^1H NMR (CD_2Cl_2 at 25 °C): δ 5.62 (br, H$_a$), 5.15 (m, H$_b$). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): δ 172.7, 164.0 (br, PPh(OEt)$_2$), 19.74 (s, $C_6H_5PO(OEt)_2$).

[16] The reaction between **1** and H_2 was also studied by NMR spectra and only showed the appearance of free nitrile signals and of **4** in the initial course of the reaction. However, the dihydride $[CoH_2P_4]^+$ cation also began to appear, in addition to free $C_6H_5PO(OEt)_2$, as the reaction proceeded, and its concentration also increased after the end of the reaction, while that of **4** decreased. The formation of $[CoH_2P_4]^+$ is not surprising, taking into account both the instability of $[CoH_2P_3\{\eta^2\text{-}C_6H_5PO(OEt)_2\}]^+$ (**4**) in solution, which can decompose liberating free phosphite, and the lability of the $\eta^2\text{-}C_6H_5PO(OEt)_2$ ligand in **4**, which can be substituted by PPh(OEt)$_2$, giving the final dihydride $[CoH_2P_4]^+$ derivative.

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