ORGANOMETALLICS

Low-valent cyanocobaltate chemistry. 1. Synthesis, characterization and reactivity of (K-Crown)[CoCp(CO)(CN)]

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Organometallics, **1985**, 4 (1), 197-198• DOI: 10.1021/om00120a034 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Organometallics **1985**, *4*, 197–198

manganese nucleus and slow quadrupole relaxation.[16]

Protonation of 1 with $NH_4^+PF_6^-$ in the presence of excess trimethyl phosphite leads to the formation of *cis*-$Mn(dmpe)_2[P(OCH_3)_3]_2PF_6^-$, **3**, in high yield.[17,18] In this reaction, the phosphite molecules fill the coordination sites vacated by pentadiene, and **2** is not produced. The cis orientation of the trimethyl phosphite ligands is evident from the $^{13}C\{^1H\}$ and ^1H NMR spectra of **3**.[18] The $^{13}C\{^1H\}$ NMR spectrum exhibits a complex series of resonances for the dmpe methyl carbon nuclei, two distinct sets of multiplets for the dmpe methylene carbon nuclei, and a virtual triplet for the trimethyl phosphite carbon nuclei.[19] The ^1H NMR spectrum consists of a complex series of resonances for the dmpe protons and a sharp doublet for the trimethyl phosphite protons (J_{P-H} = 10 Hz).[20]

Reactions of 1 with $NH_4^+PF_6^-$ in the presence of other phosphine and phosphite ligands are currently under investigation in our laboratories.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Additional support was provided by BRSG S07 RR07054-19 awarded by the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health, and by Monsanto Co. We thank Professor G. G. Stanley (Washington University) for assistance with the single-crystal X-ray diffraction study of 1.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, observed and calculated structure factor amplitudes, and significant least-squares planes including subtended dihedral angles (12 pages). Ordering information is given on any current masthead page.

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(16) Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, 1977; pp 225–226.

(17) In a typical reaction, 0.56 g (3.43×10^{-3} mols) of $NH_4^+PF_6^-$ in tetrahydrofuran was added dropwise to a solution of 1.45 g (3.43×10^{-3} mol) of **1** and 4.26 g (3.43×10^{-2} mol) of $P(OCH_3)_3$ in tetrahydrofuran maintained at −78 °C. The solution was warmed to room temperature and stirred for 12 h. The product **3** was isolated in the same manner as **2**: yield of crude product, 2.32 g (90.4%); yield of crystallized product, 2.16 g (84.2%). All manipulations were carried out under N_2.

(18) ^1H NMR (22 °C, methylene-d_2 chloride, 100 MHz): δ 1.17–1.50 (complex m, dmpe), 3.64 (d, J_{P-H} = 10 Hz, phosphite). $^{13}C\{^1H\}$ NMR (22 °C, acetonitrile-d_3, 25.14 MHz): δ 21.7–24.0 (complex m, dmpe methyl), 30.1–31.6 (m, dmpe methylene), 33.2–34.1 (m, dmpe methylene), 53.6 (virtual triplet, J = 5.7 Hz, phosphite). $^{31}P\{^1H\}$ NMR (22 °C, methylene chloride, 40.25 MHz, referenced to $P(CH_3)_3$): δ 118.8, 131.5 (br), −82.96 (heptet, J_{P-F} = 712 Hz). IR (methylene chloride): 1422, 1268, 938, 898 (CH bend, PC stretch), 1071, 1031 (POC stretch/bend), 848 cm^{-1} (PF stretch).

(19) (a) The virtual triplet in the $^{13}C\{^1H\}$ NMR spectrum is not inconsistent with a cis coordination geometry: see ref 16, p 223, and references cited therein. (b) In *trans*-$Mn(dmpe)_2[P(OCH_3)_3]_2$, all of the dmpe methyl carbon nuclei would be chemically equivalent, as would all of the dmpe methylene carbon nuclei.

(20) The ^1H NMR spectrum of *trans*-$Mn(dmpe)_2[P(OCH_3)]_2$ would be expected to exhibit a *triplet* for the trimethyl phosphite protons as a result of virtual coupling between the two magnetically inequivalent trimethyl phosphite phosphorus nuclei ($J_{PP} \gg J_{PH}$): see ref 16, p 223.

Low-Valent Cyanocobaltate Chemistry. 1. Synthesis, Characterization, and Reactivity of (K-Crown)[CoCp(CO)(CN)]†

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Received July 6, 1984

Summary: $CoCp(CO)_2$ (Cp = η^5-C_5H_5) reacts in aprotic solvents with (K-Crown)CN or (PNP)CN to give the novel complexes (K-Crown)[CoCp(CO)(CN)] and (PNP)[CoCp(CO)(CN)], whose spectroscopic and chemical properties indicate a high electron density on cobalt. In ligand exchange reactions, the cyanide dissociates exclusively, but slowly. The reactivity of the anion is dominated by its electron-transfer ability and basicity rather than its nucleophilicity.

While many compounds of the type $CpML_2$($Cp = C_5H_5$) have been characterized from the cobalt triad (L = PR_3, $P(OR)_3$, CO, CS, NO, CNR, etc.),[1] attempts to isolate complexes in which L = CN^- have to date been unsuccessful.[2,3] Although there could be many reasons for failure in these instances, it is noteworthy that only alcohols were chosen as solvents in these experiments. We assumed that the desired product might be sufficiently basic so as to be incompatible with protic solvents and that an aprotic solvent was therefore indicated.

In a recent paper,[4] we reported the development of low-valent cyanonickelate chemistry using 18-crown-6 as a solubilizing agent in aprotic media. The same strategy enables $CoCp(CO)_2$ to react with (K-Crown)CN[5] (or a combination of KCN and crown ether) at room temperature in acetonitrile, affording red-brown needles of the compound (K-Crown)[CoCp(CO)(CN)][6] (**1**) which can be isolated in better than 90% yield.

The electron-rich nature of the cobalt center is clearly in evidence from the relatively low-frequency stretches of the cyanide and carbonyl in the infrared (2066 and 1891 cm^{-1}, respectively) and the moderately upfield position of the Cp resonance in the ^1H NMR (δ 4.61). The strongly basic character of **1** is also supported by the observation that in solution it decomposes on contact with silica and that it is instantaneously protonated by trifluoroacetic acid at room temperature to give a brown uncharacterized precipitate and gas evolution. The salt is soluble in acetonitrile and DMF and sparingly soluble in THF and acetone. Compound **1**, while thermally stable, is extremely air sensitive in both solution and the solid state. The counterion of the salt can be varied by using other suitably soluble cyanides in the monosubstitution reaction, for example, PNP[CoCp(CO)(CN)][7] (**2**), which can be prepared in similar yield.

When **1** is refluxed with PPh_3 in acetonitrile or *n*-butyronitrile, equilibrium is reached after about 2 days. Product composition as established by ^1H NMR shows that only 4% of the starting material has been converted to $CoCp(CO)(PPh_3)$ (**3**) and that no CO is lost. If the phosphine complex is employed as the starting material, about 66% of **1** can be isolated following the same set of reaction conditions. The half-life for this exchange at room

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† Dedicated to the memory of my mentor Professor Earl L. Muetterties, whose enthusiasm for the synthesis and study of novel types of compounds directly inspired our efforts.

(1) See for example: Kemmitt, R. D. W.; Russell, D. R. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Vol. 5, pp 145–258. Hughes, R. P. *Ibid.* p 358.

(2) Coffey, C. E. *J. Inorg. Nucl. Chem.* **1963**, *25*, 179.

(3) Dineen, J. A.; Pauson, P. L. *J. Organomet. Chem.* **1972**, *43*, 209.

(4) del Rosario, R.; Stuhl, L. S. *J. Am. Chem. Soc.* **1984**, *106*, 1160.

(5) Crown = 18-crown-6-ether.

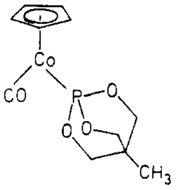
(6) **1**: mp 197–199 °C (corrected); IR (CH_3CN) 2066 (νCN, s), 1891 (νCO, s) cm^{-1}; ^1H NMR (90 MHz) δ (CD_3CN) 4.61 (s, Cp), 3.63 (s, crown ether); $^{13}C\{^1H\}$ NMR (DMF-d_7, −45 °C) δ 70.4 (s, Crown) 81.4 (s, Cp), 145.0 (s, br, CN), 211.5 (s, br, CO). Anal. Calcd for $C_{19}H_{29}NO_7CoK$: C, 47.40; H, 6.07; N, 2.91. Found: C, 47.24; H, 6.18; N, 3.00.

(7) **2**: mp 189–190 °C (corrected). Anal. Calcd for $C_{43}H_{35}N_2P_2OCo$: C, 72.07; H, 4.92; N, 3.90. Found: C, 71.49; H, 4.98, N, 4.16. The spectroscopic properties of **2** are not significantly different from **1**.

0276-7333/85/2304-0197$01.50/0

temperature is about 10 days. However, when heterogeneous conditions are employed (toluene, 24-h reflux), the yield of **3** rises to 12%. The reason for the increase is probably the insolubility of the coproduct (K-Crown)CN, which could drive the equilibrium toward the formation of **3**. If the phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane is substituted for PPh_3, the yield increases to 27%, affording the phosphite complex **4**, previously unreported.[8] The higher yield may result from the smaller cone angle of the phosphite in comparison with triphenylphosphine.

Thus it is the cyanide which dissociates exclusively from **1**. This is also illustrated by the reaction of **1** with diphenylacetylene in *n*-butyronitrile. The major products are the η^4-cyclopentadienone complex **5** (43%) and the η^4-cyclobutadiene complex **6** (~3%).[9] No significant quantities of hexaphenylbenzene are detected. Although a newly developed chromatographic material[10] allows some organocyanocobaltate products to be isolated, their total yield is very low. The remaining material may be accounted for as cobalt cyanides.[11] The chief reaction products obtained from $CoCp(CO)_2$ and diphenylacetylene are identical, although their yields are quite different (**5**, 9.5%; **6**, 46%).[12] Since toluene was employed in this experiment, the differences may be explained by the contrast in polarity or coordinating ability of the different solvents.



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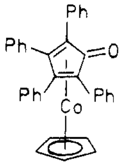

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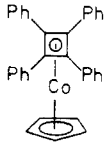

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The addition of iodine to **1** results in oxidation. The presumed product is $CoCp(CN)I_2$, since gas evolution is observed during the course of the reaction and carbonyl groups are absent from the products. The complex is thermally unstable and upon attempted isolation at room temperature decomposes to a polymeric cyclopentadienylcyanocobalt species. The same observation was noted by Dineen and Pauson,[3] who examined the reaction of $CoCp(CO)I_2$ with 1 equiv of KCN.

The oxidation of **1** by $Hg(CN)_2$ in acetonitrile at room temperature is very rapid and yields (K-Crown)CoCp$(CN)_3$[13] (95%). The reaction with $HgCl_2$ is more complicated: the formation of $CoCp(CO)_2$, cyclopentadienylcyano(chloro)cobaltates (oxidation states II and III), and polymeric cyanocobaltate species are all observed. The ability of **1** to act as an electron-transfer agent is in marked contrast to the reactivity of $CoCp(CO)_2$, with which $Hg(CN)_2$ fails to react under the same conditions[14] and mercuric halides typically produce Lewis acid–base adducts of 1:1 or other stoichiometries.[15] Another illustration of the substantial difference in redox properties between the two compounds is the observation that **1** is inert to potassium amalgam under conditions where $CoCp(CO)_2$ is reduced to a dimeric radical anion by sodium amalgam in THF.[16]

The outcome of electrophilic addition to **1** is also surprising. Synthesis of higher oxidation state isocyanide complexes through the alkylation of the corresponding cyanometalates is a well-known procedure.[17] However, the reaction of **1** with alkyl halides produces mainly paramagnetic products that have defied characterization, with evidence for the additional formation of $CoCp(CO)_2$ and Co(III) complexes in some cases, depending on the nature of the alkylating agent and solvents. Reaction with acyl halides is also generally not clean. However, with hindered acyl chlorides (RCOCl, R = *t*-Bu, 1-adamantyl), we have been able to isolate novel complexes CpCo$(CNCOR)_2$, **7** (R = *t*-Bu) and **8** (R = 1-adamantyl), in low yield. These have been characterized by IR and ^{1}H NMR spectroscopy, CI-MS, and elemental analysis.[18] To the best of our knowledge, these are the first reported compounds to contain multiple acyl isocyanide ligands. Full details of the reactions of **1** with a variety of electrophiles will be reported in a following paper.

Acknowledgment. We thank Dr. Cathy Costello at the MIT NIH Mass Spectroscopy Facility for obtaining a high-resolution mass spectrum for us. These studies are supported by the National Science Foundation Grant CHE 8209006, with additional assistance from the Biomedical Research Support Grant Program (NIH).

Registry No. **1**, 91946-70-2; **2**, 93473-81-5; **3**, 12203-85-9; **4**, 93473-82-6; **5**, 12119-11-8; **6**, 1278-02-0; **7**, 93473-83-7; **8**, 93473-84-8; $CoCp(CO)_2$, 12078-25-0; (K-Crown)CN, 42860-64-0; (PPN)CN, 65300-07-4; $CoCp(CN)I_2$, 93473-85-9; (K-Crown)CoCp$(CN)_3$, 93473-86-0; $Hg(CN)_2$, 592-04-1; diphenylacetylene, 501-65-5; 1-adamantylcarbonyl chloride, 2094-72-6; *tert*-butylcarbonyl chloride, 3282-30-2.

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[8] Red needles of **4** can be synthesized in 98% yield from $CoCp(CO)_2$ and the phosphite after a 3-h reflux in *n*-heptane: mp 204–206 °C; IR (mineral oil mull) 1944 (s), 1929 (s), 1012 (s), 961 (s), 777 (s), 658 (s) cm^{-1}; (MeCN) 1947 (s) cm^{-1}; ^{1}H NMR (90 MHz) δ (CD_3CN) 4.84 (s, Cp), 4.17 (d, OCH_2, $^3J_{PH} = 5.4$ Hz), 0.72 (s, CH_3); $^{13}C\{^1H\}$ NMR δ (CD_3CN) 75.7 (d, OCH_2, $^2J_{PC} = 8$ Hz), 83.0 (s, Cp). Anal. Calcd for $C_{11}H_{14}O_4PCo$: C, 44.01; H, 4.70; P, 10.32. Found: C, 44.10; H, 4.73; P, 10.46.

[9] Both complexes were identified by physical properties, IR and MS.

[10] Carter, S. J.; Stuhl, L. S. *J. Chromatogr.* **1984**, *291*, 348.

[11] The residual material was left on the top of silica or alumina columns as a deep blue band that could not be eluted with water/methanol. $Co(CN)_2(solvent)_2$ complexes are deep blue and air stable and interact with silica in the same way.

[12] Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888.

[13] The simple potassium salt has already been reported:[3] Other data on (K-Crown)CoCp$(CN)_3$: mp 246 °C dec; IR (mineral oil mull) 2117 cm^{-1} (s, νCN); ^{1}H NMR (CD_3CN) δ 5.20 (s), 3.63 (s). Anal. Calcd for $C_{20}H_{29}N_3O_6CoK$: C, 47.52; H, 5.78; N, 8.31. Found: C, 47.47; H, 5.73; N, 8.27.

[14] On refluxing in acetonitrile for a few hours, reaction does occur to give a mixture of oxidized products. IR spectroscopy suggests these to be cyanocobaltates (i.e., total loss of CO).

[15] Rowell, I. W.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1972**, 2393; **1972**, 2396.

[16] Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1781.

[17] Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 216.

[18] **7**: mp 63–64 °C; IR (mineral oil mull) 2017 (s, ν_{CN}), 1922 (s, ν_{CN}), 1716 (s, ν_{CO}), 1700 cm^{-1} (s, ν_{CO}); ^{1}H NMR (C_6D_6) δ 4.70 (s, 5 H, Cp), 1.09 (s, 18 H, *t*-Bu); CI (CH_4)-MS, *m/e* [relative intensity] 375 [11.7%, $(M + C_2H_5)^+$], 347 (100, $(M + H)^+$], 346 [54.2, M^+], 290 [1.0, $(M + H - C_4H_9)^+$], 263 [15.5, $(M + 2H - COC_4H_9$ or $M - C_4H_9 - CN)^+$]. Anal. Calcd for $C_{17}H_{23}N_2O_2Co$: C, 58.96; H, 6.69; N, 8.09. Found: C, 59.13; H, 6.72; N, 8.05. **8**: mp 130–131 °C; IR (mineral oil mull) 2032 (sh), 2011 (s, ν_{CN}), 1913 (s, ν_{CN}), 1708 (s, ν_{CO}), 1688 cm^{-1} (s, ν_{CO}); ^{1}H NMR (C_6D_6) δ 4.78 (s, 5 H, Cp), 1.89 (s, 9 H), 1.53 (s, 6 H); CI(CH_4)-MS, *m/e* [relative intensity] 531 [0.3%, $(M + C_2H_5)^+$], 503 [4.1, $(M + H)^+$], 502 [2.0, M^+], 341 [16.8, $(M + 2H - COAd$ or $M - Ad - CN)^+$], 163 [44.1, $AdCO^+$], 135 [100, Ad^+]. Anal. Calcd for $C_{29}H_{35}N_2O_2Co$: C, 69.31; H, 7.01; N, 5.57; Co, 11.72. Found: C, 68.85; H, 7.07; N, 5.52, Co, 11.45.