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Reaction of cobalt complex CpCo[.eta.3-(S,S,C')-SC(CN):C(CN)SC'H2] with trimethyl phosphite: reversible ring expansion and contraction

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mesitylene and generates the trihydride complex IrH$_3$(CO)(dppe).

In the presence of C$_2$H$_4$ (2 atm), 1 undergoes an unusual transformation leading to the formation of the 3,5-dimethylbenzyl ethylene complex Ir(η^2-C$_2$H$_4$)(CH$_2$C$_6$H$_3$(CH$_3$)$_2$)(CO)(dppe) (4) in nearly quantitative yield. Complex 4 was identified by NMR and IR spectroscopy, which clearly reveals coordination by a benzyl ligand rather than the mesityl ligand of 1.[10] The ^{13}C{^{1}H} 135° DEPT spectrum confirms the presence of the benzylic carbon as an inverted doublet of doublets ($^2J_{C-P}$ = 72, 6 Hz) at δ 8.3 ppm, while the ^{31}P{^{1}H} NMR spectrum shows evidence of two inequivalent phosphine donors and ν_{CO} establishes terminal CO coordination to Ir(I). The ^{1}H NMR spectrum reveals the presence of a bound ethylene with four different proton resonances upon coordination. On the basis of these results, we assign 4 as a five-coordinate Ir(I) complex with dppe spanning axial and equatorial positions of a trigonal bipyramid, the 3,5-dimethylbenzyl ligand occupying the other axial position, and CO and η^2-C$_2$H$_4$ ligands residing in the remaining equatorial sites. The structure has been confirmed by X-ray crystallography and will be discussed in a later report. A similar structure has been proposed for Ir(C$_2$H$_5$)(η^2-C$_2$H$_4$)(CO)(dppe), synthesized from IrH$_3$(CO)(dppe) and ethylene at 70 °C.[11] Under reduced pressure, complex 4 eliminates ethylene. The mechanism for the mesityl-to-benzyl rearrangement is under investigation and most likely involves C–H oxidative addition of a mesityl methyl group to produce a cyclometalated intermediate followed by reductive elimination of the aryl C–H bond. The latter step may require rearrangement of the cyclometalated intermediate to generate the required geometry for aryl C–H bond formation.

Under CO (1 atm) in CD$_2$Cl$_2$, complex 1 converts readily into the trimethylbenzoyl complex Ir(CO)$_2$(C(O)C$_6$H$_2$(CH$_3$)$_3$)(dppe) (5), which was characterized by NMR and IR spectroscopy.[12] On the basis of the spectroscopic results, the structure determination of the propionyl analog reported previously,[13] and theoretical arguments,[14] we assign 5 to be trigonal bipyramidal with the trimethylbenzoyl ligand occupying one of the axial positions. In contrast with 4, the Ir(I) acyl dicarbonyl complex 5 appears to be fluxional above −9 °C on the basis of equilibration of the dppe methylene protons, and the phosphorus nuclei, noted by NMR spectroscopy.

The four-coordinate Ir(I) aryl complex Ir(CO)(C$_6$H$_2$(CH$_3$)$_3$)(dppe) (1) synthesized and characterized in this study thus demonstrates interesting reaction chemistry, including aryl-to-benzyl ligand rearrangement, stereoselective oxidative addition of H$_2$ and diphenylsilane, and facile insertion of CO. Moreover, the oxidative-addition products of 1 establish the possibility of competitive reductive eliminations,[11,13] which are under investigation.

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Supplementary Material Available: Complete spectroscopic data for complexes 2–5 and crystallographic data for complex 1, including tables of data collection and refinement parameters, final positional parameters, complete bond distances and angles, and anisotropic thermal parameters (10 pages). Ordering information is given on any current masthead page.

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[10] Selected spectroscopic data for 4: IR (C$_6$D$_6$) 1955 (s) (CO) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 3.15 (m, 1 H, benzylic CH$_2$), 2.20 (s, 6 H, –CH$_3$), 2.11 (m, 2 H, η^2-C$_2$H$_4$, –P(CH$_2$)$_2$P–), 1.99 (m, 2 H, η^2-C$_2$H$_4$, –P(CH$_2$)$_2$P–), 1.50 (m, 1 H, benzylic CH$_2$), 0.98 (m, 1 H, η^2-C$_2$H$_4$), 0.79 (m, 1 H, η^2-C$_2$H$_4$) ppm; ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 28.1 (d, $^2J_{P-P}$ = 5 Hz), 21.9 (d, $^2J_{P-P}$ = 5 Hz) ppm; ^{13}C{^{1}H} 135° DEPT NMR (C$_6$D$_6$) δ 8.3 (dd, $^2J_{C-P}$ = 72, 6 Hz, benzylic CH$_2$) ppm. Anal. Calcd for C$_{38}$H$_{39}$IrIOP$_2$: C, 59.59; H, 5.13. Found: C, 58.11; H, 4.88. The unsatisfactory analysis for 4 is attributable in part to facile loss of ethylene which occurs upon drying the sample under vacuum.

[11] Deutsch, P. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1990**, *112*, 714.

[12] Selected spectroscopic data for 5: IR (CH$_2$Cl$_2$) 1986, 1935 (s) (CO), 1601 (s) (trimethylbenzoyl CO) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, 264 K) δ 2.17 (s, 3 H, *p*-CH$_3$), 1.75 (s, 6 H, *o*-CH$_3$) ppm; ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 264 K) δ 25.2 (d, $^2J_{P-P}$ = 6 Hz), 20.3 (d, $^2J_{P-P}$ = 6 Hz) ppm. Anal. Calcd for C$_{38}$H$_{38}$IrO$_3$P$_2$: C, 57.49; H, 4.44. Found: C, 57.56; H, 4.45.

[13] Deutsch, P. P.; Eisenberg, R. *Organometallics* **1990**, *9*, 709.

[14] (a) Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. Ed.; Pergamon: Oxford, U.K., 1982; Vol. 3, Chapter 19. (b) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365 and references therein.

Reaction of CpCo{η^3-(*S*,*S*,*C'*)-SC(CN)=C(CN)SC'H$_2$} with P(OMe)$_3$: Reversible Ring Expansion and Contraction

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Summary: The addition reaction of trimethyl phosphite to the bicyclic complex CpCo{η^3-(*S*,*S*,*C'*)-SC(CN)=C(CN)-SC'H$_2$} (**2**) causes ring expansion to give a six-membered metallacycle: CpCo{P(OMe)$_3$}{η^2-(*S*,*C'*)-SC(CN)=C(CN)-SC'H$_2$} (**3**). The irradiation of **3** with a high-pressure Hg lamp causes elimination of the phosphite to regenerate **2**.

Recently our research group has reported that the coordinatively unsaturated dithiolenes react with diazo compounds to give metallabicyclic 1:1 adducts, in which alkylidene groups do not insert into the metal–sulfur bond but bridge between the metal and sulfur.[1] Although there

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[1] (a) Sakurada, M.; Kajitani, M.; Dohki, K.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *423*, 141. (b) Kajitani, M.; Sakurada, M.; Dohki, K.; Suetsugu, T.; Akiyama, T.; Sugimori, A. *J. Chem. Soc., Chem. Commun.* **1990**, 19.

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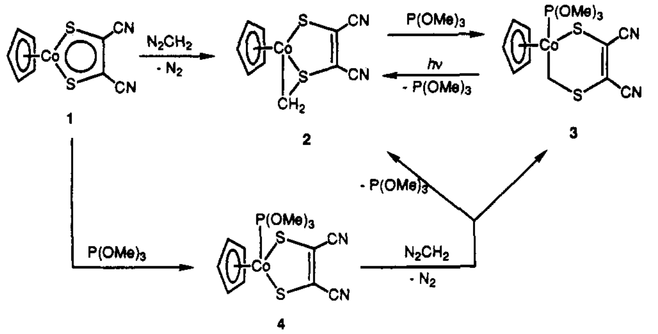
Scheme I



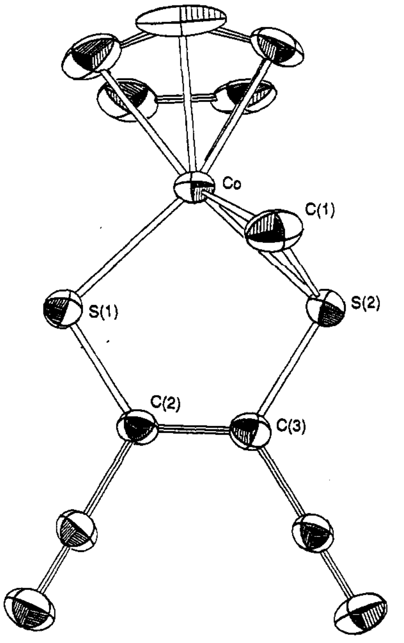


Figure 1. Molecular structure of 2. Selected bond lengths (Å) and angles (deg) are as follows: Co–C(1), 1.963 (10); Co–S(2), 2.182 (3); Co–S(1), 2.197 (3); C(1)–S(2), 1.786 (10); S(2)–C(3), 1.750 (10); S(1)–C(2), 1.702 (9); C(2)–C(3), 1.355 (12); S(1)–Co–S(2), 92.8 (1); S(2)–Co–C(1), 50.7 (3); Co–S(2)–C(1), 58.3 (3); Co–C(1)–S(2), 71.0 (3).

has been growing interest recently in carbene insertions into metallacycles,[2] examples of carbene-inserted metallacycles are rare. Now we report a new mode of carbene insertion reaction into a metallacycle and reversible ring expansion and contraction: the bicyclic methylene-added complex CpCo{η^3-(S,S,C')-SC(CN)═C(CN)SC′H$_2$} (2) reacts with trimethyl phosphite to give a ring-expanded metallacycle, CpCo{P(OMe)$_3$}{η^2-(S,C')-SC(CN)═C(CN)-SC′H$_2$} (3), which undergoes photodissociation to regenerate 2 (Scheme I).

To a solution of bicyclic compound 2 (278 mg, 1.00 mmol)[1] in methanol (100 cm^{-3}) was added a solution of trimethyl phosphite (137 mg, 1.10 mmol) in methanol (10 cm^{-3}). The mixture was stirred at room temperature for 3 h; during that time the color of the solution changed from red to brown. Filtration and recrystallization from methanol gave a 97% yield (389 mg, 0.967 mmol) of 3 as brown crystals.[3] Complex 3 was also prepared from the reaction of trimethyl phosphite-adduct 4 (51.0 mg, 0.131 mmol)[4] with a 10-fold excess of diazomethane. This reaction yielded 10% 3 (5.3 mg, 0.013 mmol) and 72% complex 2 (25.9 mg, 0.0932 mmol). Complex 3 was isolated as slightly air-sensitive microcrystals, and the structure was determined by X-ray diffraction.

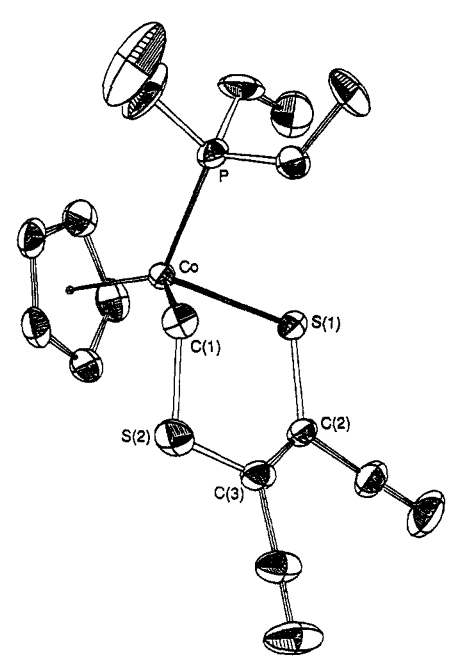


Figure 2. Molecular structure of 3. Selected bond lengths (Å) and angles (deg) are as follows: Co–C(1), 2.011 (8); Co–S(1), 2.220 (2); Co–P, 2.136 (2); C(1)–S(2), 1.789 (8); S(1)–C(2), 1.736 (7); S(2)–C(3), 1.744 (8); C(2)–C(3), 1.334 (11); C(1)–Co–S(1), 89.6 (2); C(1)–Co–P, 89.6 (2); S(1)–Co–P, 92.2 (1); Co–C(1)–S(2), 113.6 (4); Co–S(1)–C(2), 108.3 (2); C(1)–S(2)–C(3), 104.7 (4); S(1)–C(2)–C(3), 130.7 (6); S(2)–C(3)–C(2), 129.3 (6).

The structures of complexes 2 and 3 are shown in Figures 1 and 2 together with selected bond lengths and angles.[5] The structure of 2 is similar to that of the related alkylidene adduct.[1] The attack of trimethyl phosphite on the cobalt atom of complex 2 breaks the Co–S(2) bond to give the six-membered metallacycle, which forms a half-chair conformation. The central Co atom of complex 3 is at the top of a triangular pyramid, which consists of P, S(1), and C(1), and is coordinatively saturated; the complex forms a three-legged piano-stool structure. The bond

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(3) Dec pt: 142–143 °C. Anal. Calcd for $C_{13}H_{16}N_2O_3PS_2Co$: C, 38.81; H, 4.01; N, 6.96. Found: C, 38.96; H, 4.06; N, 6.93. UV–vis (CH_2Cl_2) [λ_{max} (ϵ)]: 278 (16 280), 384 nm (8620). IR (KBr): 2200 (s), 1455 (s), 1180 (w), 1125 (m), 1010 (s), 805 (m), 780 (m), 750 (m), 540 (m), 500 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.74 (1 H, dd, J_{PH} = 8.43 Hz, CH_2), 3.70 (9 H, d, J_{PH} = 10.99 Hz, OMe), 4.71 (1 H, dd, J_{PH} = 5.86 Hz, CH_2), 4.97 (5 H, s, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 9.1 (J_{CH} = 148.6 Hz, J_{PC} = 31.7 Hz, CH_2), 53.8 (J_{PC} = 6.1 Hz, OCH_3), 90.4 (J_{PC} = 2.4 Hz, C_5H_5), 115.9 (J_{PC} = 2.5 Hz, dithiolene ring carbon), 116.5 (CN), 118.6 (CN), 123.3 (J_{PC} = 4.8 Hz, dithiolene ring carbon). MS (EI, 70 eV) [m/z (relative intensity)]: 278 [14, $CpCo(CH_2)S_2C_2(CN)_2$], 264 [72, $CpCoS_2C_2(CN)_2$], 188 (29, $CpCoS_2$), 124 [100, CpCo and $P(OMe)_3$].

(4) Henderson, S. D.; Stephenson, T. A.; Wharton, E. J. *J. Organomet. Chem.* **1979**, *179*, 43.

(5) X-ray diffraction data were collected using a Rigaku AFC-5 automated four-circle diffractometer, with Mo Kα radiation graphite monochromatized (λ = 0.710 73 Å). Data for CpCo{η^3-(S,S,C')-SC(CN)═C-(CN)SC′H$_2$} (2): MW = 278.23, triclinic; $P\bar{1}$; a = 8.366 (2) Å, b = 9.319 (1) Å, c = 7.564 (1) Å, α = 94.43 (12)°, β = 109.23 (14)°, γ = 93.72 (18)°; V = 552.6 Å^3; Z = 2; d_{calcd} = 1.62 g cm^{-3}; no. of reflections = 1588 (2θ < 60°, $|Fo| \geq 3\sigma(F_o)$); R = 0.0647; R_w = 0.0687. Data for CpCo{P-(OMe)$_3$}{η^2-(S,C')-SC(CN)═C(CN)SC′H$_2$} (3): MW = 402.30, monoclinic; $P2_1/a$; a = 13.168 (3) Å, b = 13.720 (4) Å, c = 9.376 (3) Å, β = 90.20 (2)°; V = 1693.8 Å^3; Z = 4; d_{calcd} = 1.578 g cm^{-3}; no. of reflections = 2467 (2θ < 50°, $|F_o| \geq 3\sigma(F_o)$); R = 0.0537; R_w = 0.0711. The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares method. The weighting scale was $w = 1/(\sigma^2F)$.

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length of C(2)–C(3) is 1.334 (11) Å, which shows its double-bond character. The length of Co–P [2.136 (2) Å] is much shorter than that of the trimethyl phosphite–cobalt complex $[Co\{P(OMe)_3\}_4(S_2CNC_5H_{10})](BF_4)_2$ [Co–P = 2.206 and 2.244 Å (average)][6] and is shortest among those of the several trialkylphosphine–cobalt complexes (Co–P = 2.138–2.292 Å).[7]

Complex 3 undergoes facile photodissociation under irradiation with a high-pressure mercury lamp in benzene to regenerate the ring-contracted complex 2. Complex 2 is stable against irradiation under these conditions. This photodissociation occurs both under argon and in the presence of air; a ^{1}H NMR study showed that the photoreaction did not give methyl phosphate. This is different from the photodissociation of a phosphine adduct[8] or a phosphite adduct via the elimination of the coordinated phosphine by singlet oxygen to give the phosphine oxide or the phosphate, respectively.

Complex 2, therefore, causes reversible ring expansion and contraction in the processes of reaction with phosphite and during photoirradiation, as shown in Scheme I. These ring conversions occur so as to keep the coordinative saturation of the central cobalt(III) atoms and therefore so as to keep the 18-electron rule through the addition and dissociation.

An investigation involving preparing related compounds of the six-membered metallacycles is in progress.

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Supplementary Material Available: For 2 and 3, text giving full details of the preparation and characterization of the compounds and details of the structure determination, listings of crystal data, positional and thermal parameters, and bond distances and angles, and a figure showing atom numbering (23 pages). Ordering information is given on any current masthead page.

OM920174S

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(7) Orpen, A. G. *Organometallics* 1990, *9*, 1206.

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$Et_3NH^+Co(CO)_4^-$: Hydrogen-Bonded Adduct or Simple Ion Pair? Single-Crystal Neutron Diffraction Study at 15 K

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Summary: $Et_3NH^+Co(CO)_4^-$ contains a short N–H···Co contact, which provides the closest approach between the anion and cation. Accurate structural characterization by neutron diffraction at 15 K shows the N–H···Co interaction to be linear with a long N–H bond length and a relatively short Co···H separation (Co···H = 2.613 (2) Å, N–H = 1.054 (1) Å, N–H···Co = 180.0°). This evidence is consistent with the presence of a three-center–four-electron hydrogen-bond-like N–H···Co interaction, though it does not rule out simple electrostatic attraction as the principal driving force behind association of the Et_3NH^+ and $Co(CO)_4^-$ ions.

It has recently been proposed[1] that certain electron-rich transition-metal centers may be able to participate in interactions with hydrogen atoms to form three-center–four-electron (3c–4e) Z–H···M (Z = C, N) hydrogen bridges. Such interactions appear to be analogous to those of hydrogen bonds involving main-group elements, i.e., attractive interactions involving both an orbital contribution (the 3c–4e interaction) and an electrostatic contribution. The unusual aspect of these interactions is that a transition-metal atom acts as the hydrogen bond acceptor. It has been previously noted that the characteristics of such Z–H···M interactions are as follows: (i) the bridging hydrogen is reasonably protonic in nature (typically belonging to a N–H or X–C–H group, where X is an electron-withdrawing substituent), facilitating an electrostatic component to the interaction; (ii) the metal atom involved is electron-rich with filled d orbitals suitably oriented to facilitate the 3c–4e interaction involving the hydrogen atom; (iii) the ^{1}H NMR chemical shift of the bridging hydrogen atom is *downfield* of TMS and shifted *downfield* relative to the signal for the free ligand of which the hydrogen atom in question is a part; (iv) intermolecular Z–H···M linkages have an approximately linear geometry. These characteristics are analogous to those of conventional hydrogen bonds but are unlike those of three-center–two-electron (3c–2e) interactions involving transition metals, such as agostic[2] C–H→M bridges. Most examples of apparent 3c–4e Z–H···M interactions previously cited[1] have involved square-planar d^8 metal centers. Here we

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