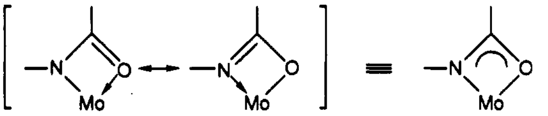
Organometallics **1992,** *11,* 2335–2337 2335

length of 1.29 (2) Å, which is longer than the corresponding bond length of free *N*-methylacetamide (1.225 Å), and a C(1)–N bond length of 1.35 (2) Å, which is slightly shorter than that of the free ligand (1.386 Å). The Mo–N distance of 2.25 (1) Å for **2a** is shorter than the average value of the σ-donating Mo–N bond distance of 2.33 Å,[13] whereas the Mo–O distance (2.24 (1) Å) is close to those of the related complex [MoH(O_2COEt-*O,O'*)(dppe)$_2$] (2.271 (2) and 2.333 (3) Å).[10] These structural features strongly suggest the following resonance form of the η^2-amide ligand of **2**:



In contrast to the thermal instability of the formamido complexes **2c** and **2d** (**2d** releases aniline, giving [Mo(CO)$_2$(dppe)$_2$] upon heating at 180 °C in vacuo), the rest of the amido complexes **2** are thermally stable both in the solid state and in solution.[14] They are, however, found to be susceptible to the electrophilic attack by organic acids. The reaction of **2f** with acetic acid in benzene at room temperature gave [MoH(O_2CCH_3-*O,O'*)(dppe)$_2$][9] together with *N*-phenylbenzamide, while that of **2b** with hexafluoroacetylacetone under similar conditions afforded [MoH{CH($COCF_3$)$_2$-*O,O'*}(dppe)$_2$] and *N*-phenylacetamide. Methanol reacted with **2** to give the formaldehyde complex [MoH$_2$(OCH$_2$)(dppe)$_2$][15] (**4**) together with the corresponding amides. A labeling experiment using CH_3OD and CD_3OD[16] revealed that the reaction proceeds as shown in Scheme III, where a β-hydrogen elimination process from the methoxo intermediate is involved. Although the reduction of transition-metal complexes with alcohol has long been known,[17] this result provides a rare example of trapping aldehyde formed by the reaction.[18]

Acknowledgment. T.I. thanks the Iwatani Scholarship and Shinsei-Shigen Kyokai for financial support.

Supplementary Material Available: Tables which contain reaction conditions and physical and spectral properties for 1 and 2, tables of crystal data, bond distances and angles, and fractional coordinates and anisotropic thermal parameters for [MoH{N(COCH$_3$)CH$_3$}(dppe)$_2$] (**2a**), and a figure giving an additional view of **2a** (10 pages). Ordering information is given on any current masthead page.

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(13) Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 3, p 1100.

(14) The melting points of complexes 2 except 2c and 2d are in the range 179–241 °C under a vacuum. These complexes tolerated heating in toluene with reflux for 5 h under a nitrogen atmosphere.

(15) [MoH$_2$(OCH$_2$)(dppe)$_2$] (4): IR (KBr) ν_{Mo-H} = 1800 (br, m), $\nu_{formyl\ C-H}$ = 2800 (m) cm^{-1}; ^{1}H NMR (270 MHz, C_6D_6) δ −2.99 (quint, 2 H, J_{H-P} = 34.63 Hz); ^{13}C NMR (78.8 MHz, C_6D_6) δ 64.11 (t, O=*C*H$_2$, J_{C-H} = 167.2 Hz); ^{31}P{^{1}H} NMR (36.5 MHz, C_6D_6, chemical shifts are in ppm with downfield positive from the external benzene solution of PPh$_3$) 71.3 (br, s).

(16) The reactions were followed by ^{1}H NMR spectroscopy. When **2b** and CD_3OH were mixed, a hydrido signal assignable to [MoH$_2$(OCD$_2$)(dppe)$_2$] appeared at first, the intensity of which then gradually decreased. In the reaction between **2b** and CD_3OD, signals due to **2b** and [MoHD(OCD$_2$)(dppe)$_2$], which were observed at the very early stages of the reaction, decreased gradually and disappeared completely after 1 h, leaving signals solely assignable to N(D)C_6H_5C(O)CH$_3$ and [MoD{N(C_6H_5)C(O)CH$_3$}(dppe)$_2$].

(17) Arnold, D. P.; Bennet, M. A. *Inorg. Chem.* **1984,** *23,* 2110.

(18) Green, M. L. H.; Parkin, G.; Moynihan, K. J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984,** 1540.

Synthesis, Structure, and Reactivity of the Four-Coordinate Aryl Complex Ir(CO)(2-mesityl)(dppe), Which Displays an Unusual Aryl to Benzyl Rearrangement

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Summary: The synthesis, structure, and reaction chemistry of Ir(CO)(2-mesityl)(dppe) (1; dppe = 1,2-bis(diphenylphosphino)ethane) is described. Complex 1 is prepared from the reaction of 2-mesitylmagnesium bromide and IrBr(CO)(dppe). The molecular structure of 1 in the solid state is that of a nearly square-planar four-coordinate complex with cis phosphine donors, a σ-bound mesityl ligand, and a slight tetrahedral distortion. Complex 1 reacts readily with diphenylsilane and H_2 to yield the respective cis oxidative-addition products IrHY(C_6H_2(CH_3)$_3$)(dppe), where Y = Ph$_2$HSi, H. A unique transformation occurs when 1 is heated in the presence of ethylene at 90 °C in benzene to yield Ir(CO)(η^2-C_2H_4)(3,5-dimethylbenzyl)(dppe). The reaction of 1 with CO generates the acyl complex Ir(CO)$_2$(C(O)mesityl)(dppe).

The reactions of small molecules with four-coordinate d^8 metal centers play a major role in homogeneous catalysis, including hydrogenation, hydroformylation, and hydrosilation.[1] For the study of these reactions mechanistically, iridium complexes such as *trans*-IrCl(CO)(PPh$_3$)$_2$ (Vaska's complex) have been useful as model systems for elucidating substrate activation via oxidative addition and adduct formation.[2,3] From our laboratory, studies have employed the bis(phosphine) complex IrX-

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 10, p 621, and references therein. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; Chapter 28, and references therein.

(2) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1961,** *83,* 2784.

(3) (a) Vaska, L. *Acc. Chem. Res.* **1968,** *1,* 335. (b) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1962,** *84,* 679. (c) Vaska, L. *Science* **1963,** *140,* 809. (d) Collman, J. P.; Kang, J. W. *J. Am. Chem. Soc.* **1967,** *89,* 844. (e) Vaska, L. *Acc. Chem. Res.* **1976,** *9,* 175. (f) Kubota, M.; Blake, D. M. *J. Am. Chem. Soc.* **1971,** *93,* 1368. (g) Blake, D. M.; Kubota, M. *Inorg. Chem.* **1970,** *9,* 989. (h) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966,** *88,* 3511. (i) Halpern, J. *Acc. Chem. Res.* **1970,** *3,* 386.

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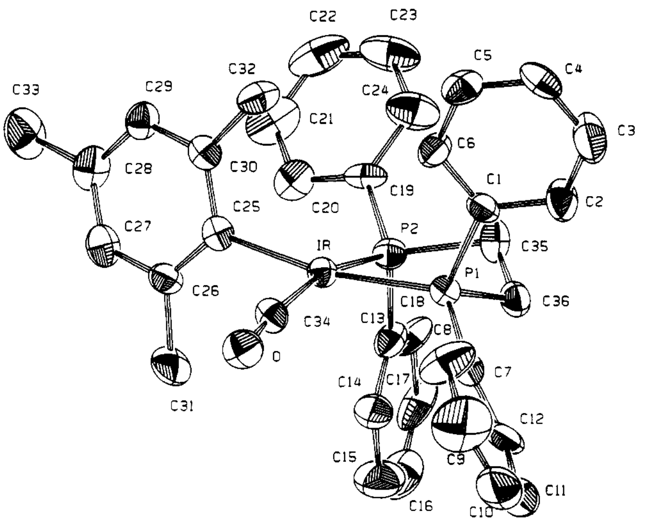
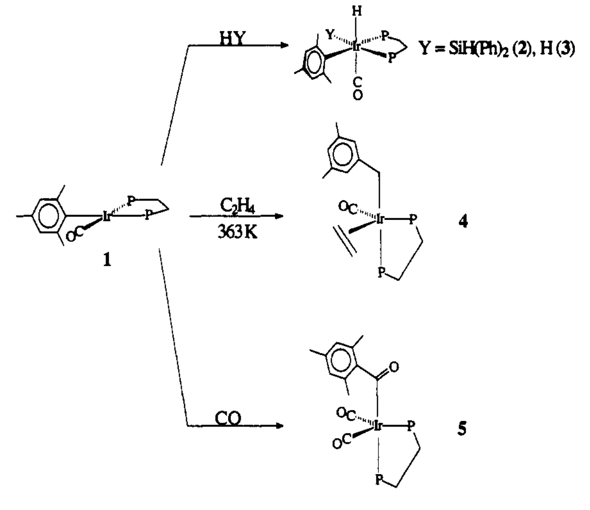


Figure 1. ORTEP representation of 1, with thermal ellipsoids shown at 35% probability. Selected bond distances (Å) and angles (deg) are as follows: Ir–P(1), 2.280 (3); Ir–P(2), 2.328 (3); Ir–C(25), 2.12 (1); Ir–C(34), 1.84 (1); O–C(34), 1.13 (1); C(25)–C(26), 1.37 (1); C(25)–C(30), 1.41 (1); C(26)–C(31), 1.51 (2); C(30)–C(32), 1.50 (1); P(1)–Ir–P(2), 83.0 (1); P(1)–Ir–C(25), 167.8 (3); P(1)–Ir–C(34), 95.1 (4); P(2)–Ir–C(25), 89.8 (3); P(2)–Ir–C(34), 164.0 (4); C(25)–Ir–C(34), 94.5 (4); Ir–C(34)–O, 173 (1). $R = 0.032$; $R_w = 0.033$.

(CO)(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane), where the phosphine donors are necessarily cis, to examine and establish the stereoselectivity and kinetic control of H_2, Si–H, and H–X oxidative addition.[4] Analogs of Vaska's complex containing alkyl, aryl, and alkoxy ligands in place of chloride have also been investigated.[5] Herein we describe the synthesis, structure, and reaction chemistry of an Ir(I) dppe complex containing a mesityl ligand which undergoes an unusual transformation to benzylic coordination. The complex oxidatively adds H–H and Si–H bonds and readily binds and inserts CO.

The complex Ir(CO)(2-mesityl)(dppe) (1; mesityl = 1,3,5-dimethylphenyl) is obtained by treating a tetrahydrofuran solution of IrBr(CO)(dppe) with two equiv of 2-mesitylmagnesium bromide at 0 °C under N_2. After neutralization of excess Grignard reagent, the product is isolated and recrystallized from EtOH/Et_2O in 69% yield as orange, air-stable microcrystals. Complex 1 has been characterized by spectroscopy, by microanalysis,[6] and by single-crystal X-ray diffraction. The solution infrared spectrum of 1 in benzene exhibits a single ν_{CO} signal at 1968 cm^{-1} indicative of terminal CO bound to Ir(I), while the $^{31}P\{^1H\}$ NMR spectrum of 1 shows two doublets at δ 49.06 and 46.52 ppm ($^2J_{P-P} = 9.7$ Hz) consistent with two inequivalent, cis-phosphorus nuclei. In the ^1H NMR spectrum, the *o*- and *p*-methyl groups of the mesityl ligand are seen as two singlets at δ 2.50 and 2.36 ppm in a 6:3 intensity ratio, respectively, while the dppe methylene protons appear as two multiplets at δ 1.81 and 2.00 ppm. For the aromatic protons, two sets of dppe ortho phenyl protons are found at δ 7.80 and 7.26 ppm, while the dppe meta and para phenyl protons, as well as the meta mesityl protons, exhibit overlapping signals between δ 7.09 and 6.86 ppm. From these results, we assign 1 as a four-coordinate Ir(I) complex containing a σ-bound mesityl ligand.

Scheme I



The structure determination of 1 using crystals grown from toluene solution confirms the above assignment as illustrated in Figure 1. The four-coordinate complex deviates from ideal square-planar geometry, as shown by the bond angles P(1)–Ir–P(2) = 83.0 (1)°, P(1)–Ir–C(25) = 167.8 (3)°, and P(2)–Ir–C(34) = 164.0 (4)° and a dihedral angle of 18.2° between the planes defined by P(1)–Ir–P(2) and C(25)–Ir–C(34), indicative of slight tetrahedral distortion. These deviations apparently reduce the steric interactions between the dppe phenyl rings on P(2) and the *o*-methyl groups of the coordinated mesityl ligand.

The reaction chemistry of 1 is depicted in Scheme I. Complex 1 undergoes oxidative-addition reactions with diphenylsilane and H_2 to afford complexes 2 and 3. The addition of 1.1 equiv of SiH_2Ph_2 to a toluene solution of 1 at 0 °C yields $IrH(SiHPh_2)(CO)(mesityl)(dppe)$ (2), which is isolated as an off white solid in 65% yield upon addition of EtOH and solvent removal.[7] There are three inequivalent mesityl methyl resonances in the room-temperature ^1H NMR spectrum, indicating hindered rotation around the mesityl–iridium bond. The reaction of 1 with H_2 (550 Torr) leads to the formation of the dihydride complex 3 quantitatively at −20 °C in CD_2Cl_2.[8] The cis-dihydride forms by stereoselective oxidative addition of H_2 over the P–Ir–CO axis of 1,[4b,9] resulting in one hydride ligand being trans to a phosphine donor and the other being trans to CO as determined by ^1H and ^{13}C NMR spectroscopy. Above −20 °C, 3 reductively eliminates

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(4) (a) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772. (b) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148. (c) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531.

(5) (a) Rees, W. M.; Churchill, M. R.; Li, Y.-J.; Atwood, J. D. *Organometallics* **1985**, *4*, 1163. (b) Schwartz, J.; Cannon, J. B. *J. Am. Chem. Soc.* **1972**, *94*, 6226. (c) Dahlenburg, L.; Nast, R. *J. Organomet. Chem.* **1976**, *110*, 395. (d) Jordan, B. F.; Harris, A. H.; Nainan, K. C.; Sears, C. T. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1451. (e) Rausch, M. D.; Moser, G. A. *Inorg. Chem.* **1974**, *13*, 11. (f) Bernard, K. A.; Atwood, J. D. *Organometallics* **1989**, *8*, 795. (g) Thompson, J. S.; Bernard, K. A.; Rappoli, B. J.; Atwood, J. D. *Organometallics* **1990**, *9*, 2727. (h) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Organometallics* **1988**, *7*, 1939.

(6) Anal. Calcd for $C_{36}H_{35}IrOP_2$: C, 58.60; H, 4.78. Found: C, 58.32; H, 4.81.

(7) Selected spectroscopic data for 2: IR (KBr) 1968 (s) cm^{-1} (CO); ^1H NMR (400 MHz, C_6D_6) δ 5.76 (m, 1 H, Si–H), 2.46 (s, 3 H, $-CH_3$), 2.25 (s, 3 H, $-CH_3$), 2.12 (s, 3 H, $-CH_3$), −8.42 (t, $^2J_{H-P} = 18.8$ Hz, 1 H, Ir–H) ppm; $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 22.7 (d, $^2J_{P-P} = 3$ Hz), 15.4 (d, $^2J_{P-P} = 3$ Hz) ppm. Anal. Calcd for $C_{48}H_{47}IrOP_2Si$: C, 62.45; H, 5.13. Found: C, 62.64; H, 5.12.

(8) Selected spectroscopic data for 3: ^1H NMR (CD_2Cl_2, 253 K) δ 2.26 (s, 6 H, *o*-CH_3), 2.11 (s, 3 H, *p*-CH_3), −9.93 (dd, $^2J_{H-P} = 132.0$, 12.9 Hz, 1 H, Ir–H), −10.06 (dd, $^2J_{H-P} = 28.0$, 18.8 Hz, 1 H, Ir–H) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 253 K) δ 27.5 (d, $^2J_{P-P} = 7$ Hz), 17.5 (d, $^2J_{P-P} = 7$ Hz) ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 253 K) δ 178.9 (t, $^2J_{C-P} = 4$ Hz, CO) ppm.

(9) Sargent, A. L.; Hall, M. B.; Guest, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 517.

mesitylene and generates the trihydride complex $IrH_3(CO)(dppe)$.

In the presence of C_2H_4 (2 atm), 1 undergoes an unusual transformation leading to the formation of the 3,5-dimethylbenzyl ethylene complex $Ir(\eta^2\text{-}C_2H_4)(CH_2C_6H_3(CH_3)_2)(CO)(dppe)$ (**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 $^{13}C\{^1H\}$ 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 $^{31}P\{^1H\}$ NMR spectrum shows evidence of two inequivalent phosphine donors and ν_{CO} establishes terminal CO coordination to Ir(I). The ^1H 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 $\eta^2\text{-}C_2H_4$ 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 $Ir(C_2H_5)(\eta^2\text{-}C_2H_4)(CO)(dppe)$, 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_2Cl_2, complex **1** converts readily into the trimethylbenzoyl complex $Ir(CO)_2(C(O)C_6H_2(CH_3)_3)(dppe)$ (**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 $Ir(CO)(C_6H_2(CH_3)_3)(dppe)$ (**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.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. CHE 89-09060) for support of this work, the Johnson Matthey Co., Inc., for a generous loan of iridium trichloride, and Dr. Paul Deutsch for helpful discussions. B.P.C. gratefully acknowledges Sherman Clarke and Bristol Myers-Squibb Fellowships.

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_6D_6) 1955 (s) (CO) cm^{-1}; ^1H NMR (C_6D_6) δ 3.15 (m, 1 H, benzylic CH_2), 2.20 (s, 6 H, $-CH_3$), 2.11 (m, 2 H, $\eta^2\text{-}C_2H_4$, $-P(CH_2)_2P-$), 1.99 (m, 2 H, $\eta^2\text{-}C_2H_4$, $-P(CH_2)_2P-$), 1.50 (m, 1 H, benzylic CH_2), 0.98 (m, 1 H, $\eta^2\text{-}C_2H_4$), 0.79 (m, 1 H, $\eta^2\text{-}C_2H_4$) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 28.1 (d, $^2J_{P-P}$ = 5 Hz), 21.9 (d, $^2J_{P-P}$ = 5 Hz) ppm; $^{13}C\{^1H\}$ 135° DEPT NMR (C_6D_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_2Cl_2) 1986, 1935 (s) (CO), 1601 (s) (trimethylbenzoyl CO) cm^{-1}; ^1H NMR (CD_2Cl_2, 264 K) δ 2.17 (s, 3 H, *p*-CH_3), 1.75 (s, 6 H, *o*-CH_3) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 264 K) δ 25.2 (d, $^2J_{P-P}$ = 6 Hz), 20.3 (d, $^2J_{P-P}$ = 6 Hz) ppm. Anal. Calcd for $C_{38}H_{38}IrO_3P_2$: 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 $CpCo\{\eta^3\text{-}(S,S,C')\text{-}SC(CN){=}C(CN)SC'H_2\}$ with $P(OMe)_3$: Reversible Ring Expansion and Contraction

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Summary: The addition reaction of trimethyl phosphite to the bicyclic complex $CpCo\{\eta^3\text{-}(S,S,C')\text{-}SC(CN){=}C(CN)SC'H_2\}$ (**2**) causes ring expansion to give a six-membered metallacycle: $CpCo\{P(OMe)_3\}\{\eta^2\text{-}(S,C')\text{-}SC(CN){=}C(CN)SC'H_2\}$ (**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.