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Co-Complexes Derived from Alkene Insertion to Alkyne-Dicobaltpentacarbonyl Complexes: Insight into the Regioselectivity of Pauson−Khand Reactions of Cyclopropenes

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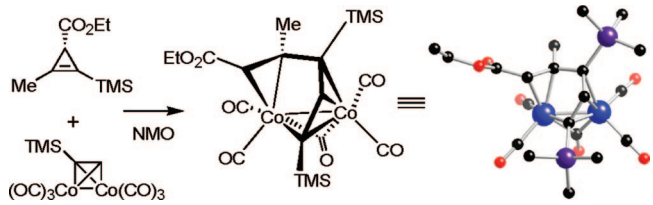

Described are the X-ray crystallographic and spectral properties of Co-complexes that were isolated from two Pauson−Khand reactions of chiral cyclopropenes. These are the first examples of isolated Co-complexes derived from the putative alkene-insertion intermediates of Pauson−Khand reactions. The binuclear Co-complexes are coordinated to μ-bonded, five-carbon "flyover" carbene ligands. It is proposed that the complexes result from cyclopropane fragmentation subsequent to alkene insertion. The observation of these metal complexes provides a rationale for the origin of regioselectivity in Pauson−Khand reactions of cyclopropenes.

Introduction

The Pauson−Khand reaction is a formal [2+2+1] cyclocarbonylation reaction that results in the formation of cyclopentenone products.[1,2] This transformation has emerged as a powerful tool for stereoselective syntheses because of the significant molecular complexity that is generated from simple starting materials.[1] Cyclopropenes are excellent substrates for Pauson−Khand reactions.[3,4] Recently, our group described general conditions for the utilization of chiral cyclopropenes in intermolecular Pauson−Khand reactions,[4b] and the enantioselective synthesis of pentalenene via an intramolecular cyclopropene Pauson−Khand reaction.[4a] In intermolecular Pauson−Khand reactions, 1,2-disubstituted cycloprop-1-enes are particularly efficient substrates. Such reactions proceed with excellent regio- and diastereoselectivity to produce cyclopentenones in good yield (57−82%). In many cases, red cobalt-containing side products were observed in the Pauson−Khand reactions of cyclopropenes. Described herein are the spectroscopic and crystallographic properties of two cobalt complexes that were isolated. Mechanistic implications of the formation of these complexes are also discussed.

According to the accepted mechanism,[5] the first intermediate in the Pauson−Khand reaction is an alkyne−$Co_2(CO)_5$ complex that results from the loss of CO ligand from an alkyne−$Co_2(CO)_6$ complex. Structural evidence for this proposal first came from Krafft and co-workers, who isolated **2** as an intermediate to cyclopentenone **3** during studies on the directed intramolecular Pauson−Khand reaction (Scheme 1).[6] A similar

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(6) Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199–7207.

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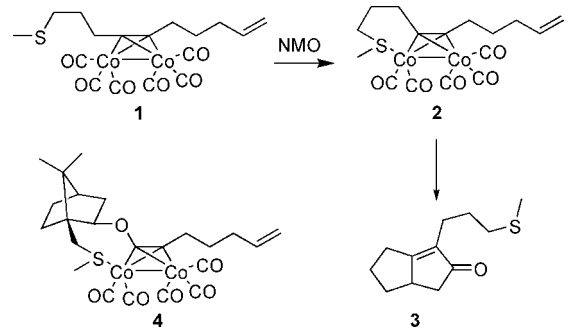
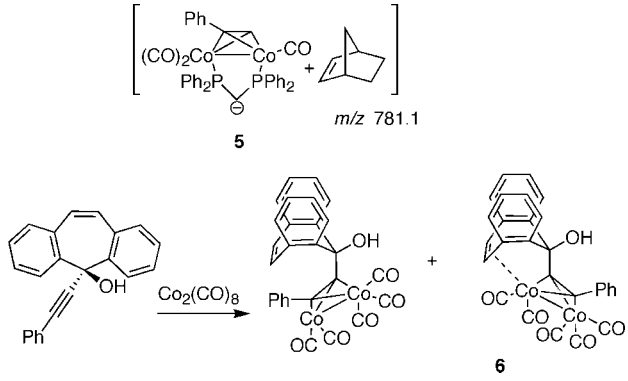
SCHEME 1. Evidence for Alkyne·$Co_2(CO)_6$ Complexes in Pauson−Khand Reactions



SCHEME 2. Evidence for Alkene Coordination to Alkyne·$Co_2(CO)_6$ Complexes

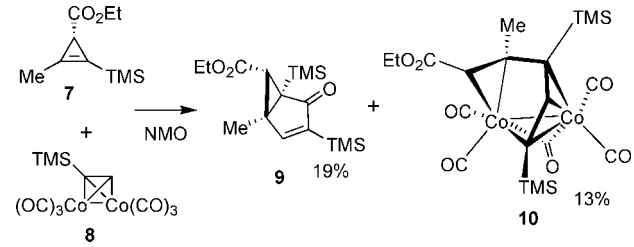


complex (**4**) was subsequently isolated by Pericás and co-workers while exploring Pauson−Khand reactions that employed tethered chiral auxiliaries.[7] Later, alkyne·$Co_2(CO)_6$ complexes were characterized by IR in studies by Gordon and co-workers.[8]

Several studies have also supported the proposal that alkene complexes of alkyne·$Co_2(CO)_6$ are intermediates in Pauson−Khand reactions. In an intermolecular Pauson−Khand reaction, Gimbert and co-workers used ESI-MS to monitor an intermolecular Pauson−Khand reaction, and detected a peak (781.1 Da) corresponding to the alkyne−Co complex **5** + norbornene.[9] More recently, Evans and McGlinchey reported the X-ray crystal structure of **6**, an alkyne−pentacarbonyl complex with an alkene coordinated in intramolecular fashion.[10] Although **6** is an alkene complex, structural constraints do not permit alkene insertion into the Co−alkyne complex (Scheme 2).

Alkene insertion has been reported to be the rate-determining step in Pauson−Khand reactions that have been studied mechanistically.[1,5,11] Thus, it has been difficult to obtain information about the intermediates that form subsequent to alkene insertion. Herein, we describe the first examples of Co-complexes derived from the putative alkene-insertion intermediate of a Pauson−Khand reaction. The complexes are binuclear,

SCHEME 3. Isolation of a Co-Complex in an Intermolecular Pauson−Khand Reaction



and they are coordinated by μ-bonded, five-carbon "flyover" carbene ligands.[12] It is postulated that these complexes result from fragmentation of the cyclopropane subsequent to the alkene insertion step. These observations provide insight into the origin of regioselectivity and the limitations of catalysis for the intermolecular Pauson−Khand reactions of cyclopropenes. Furthermore, these complexes provide indirect evidence for the alkene insertion intermediates that have been invoked in the Magnus−Schore mechanism[5] for the Pauson−Khand reaction.

Results and Discussion

In the Pauson−Khand reaction of **7** with **8**, red cobalt complex **10** accompanied formation of cyclopentanone **9** (Scheme 3). The conditions in Scheme 3 led to maximum yields of the red cobalt complex, whereas conditions previously reported (BuSMe, 100 °C) maximized the yield of the cyclopentenone.[4b] The red cobalt complex could be purified on a column of silica gel and isolated along with the cyclic enone product. While crude TLC analysis indicated that the red complex was the major product, only 13% of **10** could be isolated because of partial decomposition upon silica gel chromatography.

It was possible to obtain X-ray quality crystals for **10**. A molecular diagram of the X-ray structure of **10** and a table of selected bond distances is displayed in Figure 1. The binuclear complex is coordinated by a μ-bonded, five-carbon ligand. "Flyover" 2,4-pentadienylidene ligands of this type have been described previously for dicobalt complexes, but they were prepared by unrelated routes.[12] Structure **10** contains two ligands that bridge both cobalt atoms: a bridging carbonyl (C^8) and the bridging "flyover" carbene (C^3) of the five-carbon ligand (C^3 to C^7). Thus, C^3 is both σ-bonded to Co^1 and also a part of the allylic bond to Co^2. Bonding of Co^2 to C^4 and C^5 completes the allylic bond. Co^1 is π-bonded to C^6 and C^7.

The IR spectrum displays four peaks that are attributed to the five carbonyls of **10**. Peaks at 2067, 2038, and 2008 cm^{-1} are attributed to the terminal carbonyl ligands: the peak at 2008 cm^{-1} is roughly twice the intensity of the other carbonyls and

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(9) Gimbert, Y.; Lesage, D.; Milet, A.; Fournier, F.; Greene, A. E.; Tabet, J.-C. *Org. Lett.* **2003**, *5*, 4073–4075.

(10) Banide, E. V.; Müller-Bunz, H.; Manning, A. R.; Evans, P.; McGlinchey, M. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 2907–2910.

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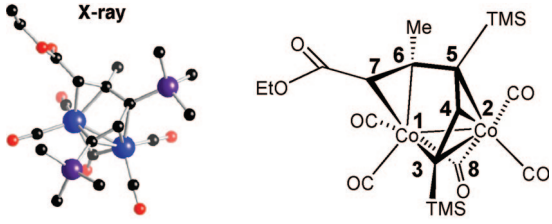
(12) Closest crystallographically characterized precedents of **10** and **18**: (a) Váradi, G.; Horváth, I. T.; Pályi, G.; Markó, L.; Slovokhotov, Y. L.; Struchkov, Y. T. *J. Organomet. Chem.* **1981**, *206*, 119–130. (b) King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1983**, *105*, 4846–4848. (c) King, J. A., Jr.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1994**, *470*, 207–222. (d) Hong, P.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1978**, *150*, 279–293.

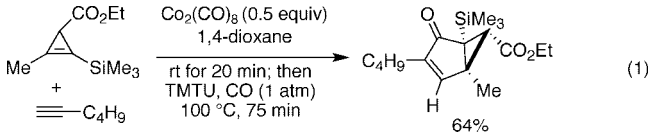


IR: ν_{CO}: 2067, 2038, 2008 1853 (bridging CO)

Selected bond lengths	Co^1–Co^2 2.46888(8) Å		Selected angles
Co^1–C^3 1.998(4) Å	Co^2–C^3 2.002(4) Å	C^3–C^4 1.428(6) Å	Co^1–C^3–Co^2 76.22(14)°
Co^1–C^8 2.094(4) Å	Co^2–C^4 2.061(4) Å	C^4–C^5 1.415(6) Å	Co^1–C^8–Co^2 79.31(18)°
Co^1–C^7 2.082(4) Å	Co^2–C^5 2.183(4) Å	C^5–C^6 1.510(5) Å	
Co^1–C^8 1.983(5) Å	Co^2–C^8 1.884(5) Å	C^6–C^7 1.413(6) Å	

FIGURE 1. X-ray crystal structure and selected properties of **10**.

is attributed to two overlapping carbonyl peaks. A peak at 1853 cm^{-1} was attributed to the bridging carbonyl. The frequency of the terminal and bridging carbonyl peaks correlates to those of related dinuclear cobalt complexes in the literature.[12a,13] The ^{13}C NMR spectrum of **10** at 25 °C contains three peaks at 197, 202, and 212 ppm that integrate with a ratio of 1:1:3, respectively (Figure 2). These peaks are associated with the carbonyls attached to the cobalt atoms. However, at −25 °C the peak at 212 ppm is not observed. Two new peaks at 230 and 206 ppm appear when the temperature is lowered to −60 °C. The new peak at 230 ppm is assigned to the bridging carbonyl.[13] For the spectrum acquired at −60 °C, the peaks at 230, 206, 203, and 198 ppm integrate with a ratio of 1:2:1:1, respectively. Our interpretation is that the exchange of the bridging and the terminal carbonyls is slow at −60 °C, but exchange between the bridging carbonyl and two of the terminal carbonyls is fast on the NMR time scale at 25 °C. Coalescence is observed at −25 °C in the ^{13}C NMR of **10**. Analogous observations have been made by Haenel and co-workers for a hexacarbonyldicobalt complex coordinated by 4,6-bis(diphenylphosphino)dibenzofuran.[13] The Haenel complex contains two, nonequivalent bridging carbonyls, and ^{13}C NMR studies on this complex demonstrated that carbonyl exchange is rapid at rt but slow at −80 °C, and that coalescence is observed at −30 °C.[13]



(1)

It was possible to utilize substoichiometric amounts of $Co_2(CO)_8$ in some of the Pauson−Khand reactions while using tetramethyl thiourea (TMTU)[14d] as the promotor of cyclopentenone (64%) formation (eq 1).[15] However, in no case was it possible to use less than 0.5 equiv of $Co_2(CO)_8$. Red side products were generally observed in the Pauson−Khand reactions of cyclopropenes. It was speculated that the formation of these side products represented a catalytically nonproductive

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(15) It was also possible to utilized substoichiometric $Co_2(CO)_8$ in the TMTU-promoted intramolecular Pauson−Khand reaction of a cyclopropenyne. See ref 4a.

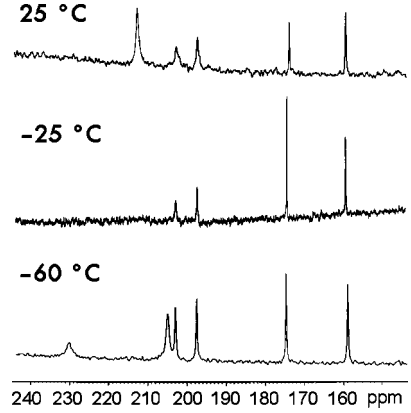
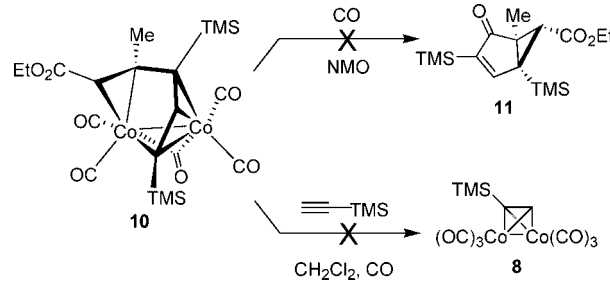


FIGURE 2. Variable-temperature ^{13}C NMR spectra of **10** (100 MHz, $CDCl_3$). Because overnight acquisition times were necessary and because **10** is only moderately stable over prolonged periods in solution, freshly prepared solutions of **10** were prepared for spectral acquisition at different temperatures. Thus, the signal-to-noise ratios differ for the three spectra displayed.

SCHEME 4. Formation of Cobalt Complex 10 Is Unproductive for Catalysis

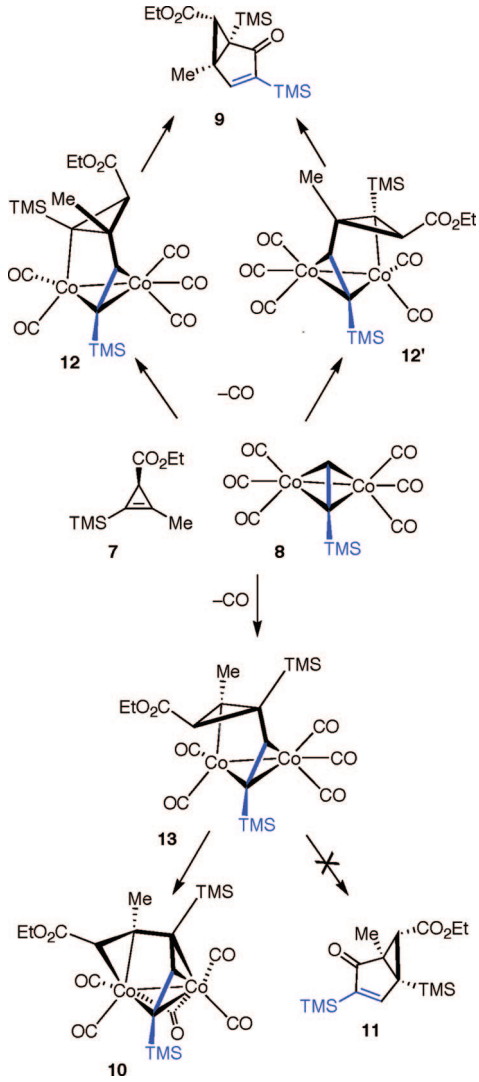


pathway by which cobalt was consumed. To support this hypothesis, **10** was treated with NMO[14a,b] under conditions that promote Pauson−Khand reactions of cyclopropenes:[4b] **10** remained unaltered and cyclopentenone **11** did not form (Scheme 4). Similarly, complex **10** did not return the alkyne complex **8** when treated with trimethylsilylacetylene under an atmosphere of CO. These experiments suggest that the formation of **10** takes cobalt out of the catalytic cycle, and provide one reason for the high catalyst loadings that are needed.

Intermolecular Pauson−Khand reactions of cyclopropenes proceed with high regioselectivity to produce cyclopentenone products.[4b] Intriguingly, the complex **10** has the opposite regioselectivity relative to the cyclopentenone product **9** (Scheme 5). It seems that the high regioselectivity in cyclopropene Pauson−Khand reactions is only partly due to the selectivity in alkene insertion. The regioselectivity is further accentuated by a kinetic discrimination after alkene insertion. Thus, the putative insertion product **13** leads to **10**, and does not produce cyclopentenone **11**. In contrast, cyclopentenone **9** arises from **12** and/or diastereomeric **12′**. It is intriguing that the putative intermediate **13** leads to reductive ring-opening, whereas the regioisomeric structures **12** lead to Pauson−Khand products. Ring-opened product **10** contains a carbon−metal bond that is α to the trimethylsilyl group that was originally bound to the cyclopropane moiety of **13**. Silicon is known to stabilize α-carbon−metal bonds.[16] This stability may be reflected in a relatively low barrier for the transformation of **13** into **10**, and provide a plausible explanation for the susceptibility of **13** to undergo reductive cleavage.

(16) Paquette, L. A. *Science* **1982**, *217*, 793.

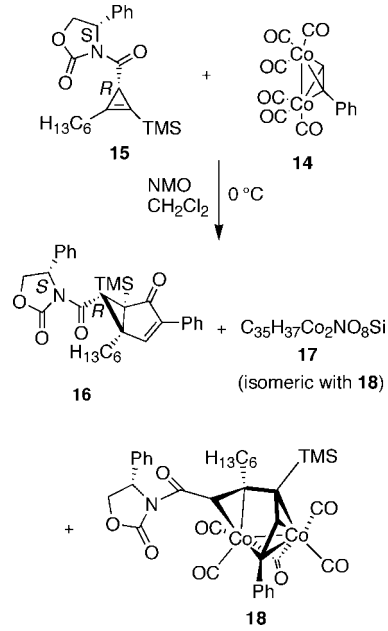
SCHEME 5. The Origin of Regiocontrol for Intermolecular Pauson−Khand Reactions



The NMO-promoted reaction of phenylacetylene complex **14** with **15** gave Co-complexes **17** (15%) and **18** (41%) along with cyclopentenone **16** (19%) (Scheme 6). The conditions in Scheme 6 led to maximum yields of the red cobalt complexes, whereas conditions previously reported (BuSMe, 100 °C) maximized the yield of the cyclopentenone.[4b] Compound **18** was characterized by X-ray crystallography and was found to be structurally similar to **10** (Figure 3). The spectral properties of compound **17** were roughly similar to those of **18**, including the observation of bridging carbonyl (1866 cm^{-1}) in the IR spectrum. However, it was not possible to unambiguously characterize **17** because it was limited in quantity. The spectral properties of cobalt complex **17** may be consistent with a structure that is regioisomeric with **18**.

In summary, red cobalt complexes were isolated as side products in the intermolecular Pauson−Khand reactions of cyclopropenes. The complexes were characterized by X-ray crystallography, ^{13}C NMR, and IR spectroscopy, and they each possess a bridging carbonyl and a five-carbon, μ-bonded "flyover" carbene ligand. These structures result from fragmentation of the cyclopropane ring after alkene insertion. A conclusion of the study is that the high regioselectivity of intermolecular cyclopropene Pauson−Khand reactions is not

SCHEME 6. Two Cobalt Complexes Formed As Side Products along with Cyclopentenone 16

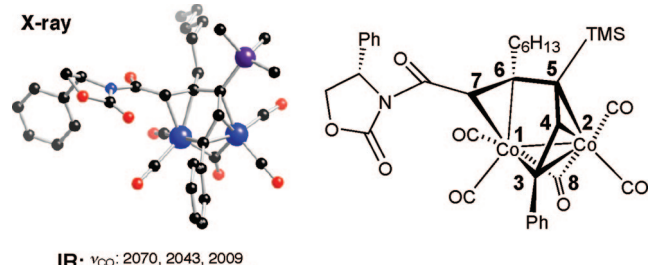


solely a consequence of selective alkene insertion. Rather, the regioselectivity is augmented by a kinetic discrimination after alkene insertion, in which only the minor diastereomer leads to the ring-opened side product. As the first characterized examples of Co-complexes derived from putative alkene insertion intermediates, these complexes provide indirect evidence for the Magnus−Schore mechanism for the Pauson−Khand reaction.

Experimental Section

The experimental procedures for the preparation of alkyne−dicobalt hexacarbonyl complexes **8** and **14** are as described in the literature.[4b] The Pauson−Khand reaction conditions that maximize the formation of red cobalt complexes are described below. The spectral data for **9** and **16** were previously reported.[4b]

General Procedure for the Formation of Red Cobalt Complexes in Intermolecular Pauson−Khand Reactions. A dry 50-mL round-bottomed flask was outfitted with a stir bar, gas inlet adapter, and a rubber septum. The assembly was flame dried under vacuum and cooled under nitrogen. The alkyne−cobalt complex (2.0 equiv) and the cyclopropene (1.0 equiv) were then added, and the apparatus was evacuated and filled with nitrogen. CH_2Cl_2 was added and the mixture was cooled by an ice-bath (0 °C). NMO (5.0 equiv) was added and the reaction mixture was allowed to stir at 0 °C for 5



Selected bond lengths						Selected angles	
Co^1–C^3	1.983(4) Å	Co^2–C^3	2.011(4) Å	C^3–C^4	1.417(6) Å	Co^1–C^3–Co^2	76.22(14)°
Co^1–C^6	2.161(4) Å	Co^2–C^4	2.057(4) Å	C^4–C^5	1.409(6) Å	Co^1–C^8–Co^2	77.59(15)°
Co^1–C^7	2.122(4) Å	Co^2–C^5	2.153(4) Å	C^5–C^6	1.501(6) Å		
Co^1–C^8	1.974(5) Å	Co^2–C^8	1.901(5) Å	C^6–C^7	1.432(6) Å		
Co^1–Co^2	2.5026(9) Å						

FIGURE 3. X-ray crystal structure and selected properties of **18**.

min. The cold bath was then removed and the mixture was allowed to stir while warming to rt for 45 min. Volatile solvents were removed under reduced pressure and the residue was chromatographed on silica gel.

Pentacarbonyl-μ-[1,3-bis(trimethylsilyl)-5-ethoxycarbonyl-4-methyl-*cis*-2,4-pentadienylidene-1(1,2,3-η^3):2(4,5-η^2)-1κC^1:2κC^1]dicobalt (Co−Co) (10). The general procedure was followed with use of **7** (255 mg, 1.29 mmol), **8** (990 mg, 2.58 mmol), NMO (1.51 g, 12.9 mmol), and CH_2Cl_2 (25 mL). Chromatography on silica gel (2% CH_2Cl_2 in hexanes) provided 81 mg (0.25 mmol, 19%) of **9**[4b] and 95 mg (0.17 mmol, 13%) of **10** as a red solid. The red cobalt complex **10** crystallized from hexanes, mp 118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 4.63 (s, 1H), 4.19−4.14 (m, 1H), 4.01−3.96 (m, 1H), 2.52 (m, 4H), 1.23 (t, J = 8.0 Hz, 3H), 0.34 (s, 9H), 0.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.5, 202.8, 197.2, 173.7, 159.2, 110.9, 106.4, 92.0, 59.9, 49.1, 24.5, 14.2, 0.2, −0.4; IR ($CHCl_3$, cm^{-1}) 2066, 2038, 2008, 1852, 1691, 1215; HRMS-EI *m*/*z* [M + Na], calcd for $C_{20}H_{28}Co_2O_7Si_2Na$ 576.9935, found 576.9940. Anal. Calcd for $C_{20}H_{28}Co_2O_7Si_2$: C, 43.32; H, 5.09. Found: C, 43.62; H, 5.03.

Cobalt Complex 17 and Pentacarbonyl-μ-{4-methyl-1-phenyl-5-[4(*S*)-4-phenyloxazolidinatocarbonyl]-3-trimethylsilyl-*cis*-2,4-pentadienylidene-1(1,2,3-η^3):2(4,5-η^2)-1κC^1:2κC^1}dicobalt (Co−Co) (18). The general procedure was followed with use of **15** (150 mg, 0.39 mmol), **14** (300 mg, 0.78 mmol), NMO (228 mg, 1.95 mmol), and CH_2Cl_2 (10 mL). Chromatography on silica gel (10% ethyl acetate in hexanes) provided 45 mg (0.06 mmol, 15%) of **17** as a red solid, 120 mg (0.161 mmol, 41%) of **18** as a red solid, and 39 mg (0.76 mmol, 19%) of **16**[4b] as a colorless semisolid. Compound **18** crystallized from hexanes. The structure of **17** could not be definitively assigned; spectral properties of **17** are listed in the Supporting Information.

Spectral properties of 18: mp 70−73 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50−7.26 (m, 10H), 5.43 (m, 1H), 4.78 (br s, 1H), 4.60 (m, 1H), 4.28 (br s, 1H), 4.17 (m, 1H), 2.67 (m, 1H), 2.43 (m, 1H), 1.51−0.81 (m, 11H), 0.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 212.3 (br), 201.6, 196.7, 172.0, 163.0, 153.5, 148.2, 139.7, 129.0, 128.4 (2 peaks), 128.3, 127.4, 125.6, 107.6, 101.5, 99.9, 69.4, 58.0, 49.8, 37.9, 32.1, 31.4, 29.4, 22.4, 14.1, 0.3; IR ($CHCl_3$, cm^{-1}) 2958, 2070, 2043, 2009, 1855, 1776, 1665, 1443, 1383, 1213; HRMS-EI *m*/*z* [M + Na], calcd for $C_{35}H_{37}Co_2NO_8SiNa$ 768.0850, found 768.0842. Anal. Calcd for $C_{35}H_{37}Co_2NO_8Si$: C, 56.38; H, 5.00; N, 1.88. Found: C, 56.22; H, 5.09; N, 1.85.

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Supporting Information Available: Full experimental details are provided, as are characterization details for all compounds, copies of ^{1}H NMR, ^{13}C NMR, and IR spectra for new compounds, and CIF files for compounds **10** and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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