Communications to the Editor

Synthesis and Structure of the First Binuclear Methylene-Bridged Cobalt Complex, $Co_2(\eta^5\text{-}Me_5Cp)_2(\mu\text{-}CH_2)(\mu\text{-}CO)$: A Surprising Role for the Lithium Enolate of Acetaldehyde

Sir:

The determination of reactivity patterns between small organic molecules and organometallic compounds and the extension of structural classes of organometallic species are fundamental aspects of the search for new homogeneous catalysts. We wish to report in this communication a novel reaction between the lithium enolate of acetaldehyde ($Li^+CH_2CHO^-$), lithium pentamethylcyclopentadienide ($Li^+Me_5Cp^-$), and cobaltous chloride ($CoCl_2$). This reaction gives rise to the first reported methylene-bridged binuclear cobalt compound, $Co_2(\eta^5\text{-}Me_5Cp)_2(\mu\text{-}CH_2)(\mu\text{-}CO)$, **1**. Several lines of evidence suggest that the two bridging groups are derived from the enolate starting material, raising the possibility of a heretofore unknown pattern of reactivity between aldehyde enolates and organo-transition-metal complexes.

The above results stemmed from an attempt to prepare bis(pentamethylcyclopentadienyl)cobalt, via the reaction of lithium pentamethylcyclopentadienide ($Li^+Me_5Cp^-$) with anhydrous cobaltous chloride ($CoCl_2$). A solution of *n*-butyllithium (10 mL, 1.65 N in hexane, 16.5 mmol) in 50 mL of tetrahydrofuran (THF) was prepared in a He atmosphere. After several minutes at room temperature, this solution was added to a THF solution of pentamethylcyclopentadiene (HMe_5Cp, 2.44 g, 16.5 mmol). Anhydrous $CoCl_2$ was then added (0.941 g, 7.2 mmol), and the resulting dark brown mixture was refluxed gently for 2 h. Solvent was removed under vacuum and the residue extracted with ~150 mL of hexane. After filtration, hexane was removed from the deep green-black solution under vacuum until the volume was reduced to ~10 mL. After several days at -20 °C, 350 mg of small blue-black crystals of the μ-CH_2 compound **1** were recovered (22% yield based on $CoCl_2$). The crystals redissolve readily in THF or hexane to give extremely air-sensitive deep royal blue solutions.

Analytical studies showed that the crystals were *not* the desired $(Me_5Cp)_2Co$.[1] Elemental analysis[2] and mass spectroscopy[3] suggested a binuclear complex with only one Me_5Cp per Co. Other spectroscopic information[3] included a strong IR band at 1758 cm^{-1}, which indicated the presence of a bridging carbonyl, and an unidentified ^1H NMR singlet at 10.68 ppm which was subsequently assigned to the bridging methylene group uncovered in the X-ray analysis. The structure determination was carried out on a single crystal[4] grown from hexane, from which 1713 independent diffracted intensities[5] were observed with $|F_o| \geq 2.0\sigma_F$.[6] The compound crystallizes ($Z = 2$) in the space group $P2/c$ (C_{2h}^4, no. 13)[7] with lattice constants $a = 9.641$ (1), $b = 8.591$ (1), and $c = 12.922$ (1) Å and $\beta = 106.36$ (1)° with $V = 1027.6$ Å^3. The final conventional residual was $R_1 = 0.054$, and the weighted residual, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0.066 with 115 parameters (14 nonhydrogen atoms and a scale factor) varied in the least-squares[9] and a data-to-parameter ratio of 14.9:1. The final difference Fourier synthesis displayed maximum residual densities of ~0.5 e Å^{-3} at positions consistent with methyl and methylene hydrogen atoms.

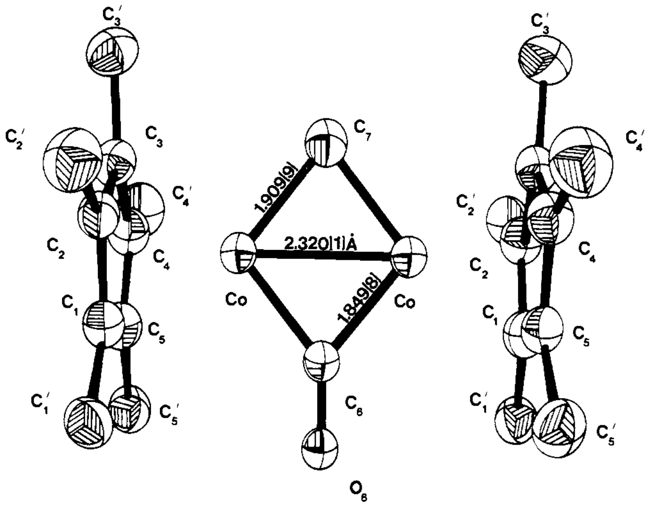

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Figure 1. ORTEP drawing of the structure of $Co_2(\eta^5\text{-}Me_5Cp)_2(\mu\text{-}CH_2)(\mu\text{-}CO)$.

The perspective view presented in Figure 1 illustrates that **1** is a binuclear compound containing two pentamethylcyclopentadienylcobalt units linked via a metal-metal bond and two bridging ligands: a carbonyl (C_6-O_6) and a methylene (C_7). The molecular geometry closely resembles that recently reported[12] for the di(μ-CO) analogue $Co_2(\eta^5\text{-}Me_5Cp)_2(\mu\text{-}CO)_2$. The metal-metal bond distance in **1** is comparable to that found in the di(μ-CO) analogue [2.320 (1) Å vs. 2.38 (2) Å]. Both distances are rea-

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[1] Subsequent to the initiation of this work, we learned of a recent successful synthesis of $(Me_5Cp)_2Co$ via reduction of $[(Me_5Cp)_2Co]PF_6$: John L. Robbins, private communication.

[2] Anal. Calcd for $Co_2C_{22}H_{32}O$: C, 61.40; H, 7.50. Found: C, 61.30; H, 7.56.

[3] ^1H NMR (benzene-d_6) δ 10.68 (s, μ-CH_2), 1.56 (s, CH_3); ^{13}C NMR (benzene-d_6) δ 190.21 (s, μ-CH_2 or μ-CO), 89.52 (s, Me_5Cp ring C), 9.29 (s, CH_3); mass spectrum, M^+ 430; a small peak at *m/e* 444 is attributed to $Co_2(Me_5Cp)_2(CO)_2$ which may be a contaminant in solid **1** or may arise from decomposition of **1** in the mass spectrometer; IR (KBr, cm^{-1}) 2970, 2915, 2858 (s, aliphatic C-H), 1758 (s, μ-CO); a small shoulder at 1746 may be due to traces of $Co_2(Me_5Cp)_2(CO)_2$.

[4] Data were collected by Molecular Structure Corp., College Station, TX. The crystal studied was sealed in a thin-walled capillary under inert atmosphere.

[5] A group of 2358 independent data were examined by using a θ-2θ scan with graphite monochromatized Mo Kα (λ = 0.71073 Å) radiation on an Enraf-Nonius CAD4 diffractometer. Intensities were not corrected for absorption [μ(Mo Kα) = 1.68 mm^{-1} with a calculated density of 1.39 g cm^{-3}], as several psi scans displayed insignificant fluctuation. Periodically monitored check reflections displayed no significant variation in intensity throughout the experiment.

[6] $|F_o| = [(C - tB)R/Lp]^{1/2}$ and $\sigma_F = {}^1/_2\{[R^2(C + t^2B)/(|F_o|Lp)^2] + (0.05|F_o|)^2\}^{1/2}$; C is the total count recorded during the scan, t = 2.0 is the ratio of the scanning time to the total background B, R is the scan rate, and L and p are the Lorentz and polarization corrections.

[7] Systematic extinctions ($l = 2n + 1$ for $h0l$) limited the possible space groups to either this one or Pc (C_s^2, no. 7). The analysis was conducted in the centrosymmetric group because attempted refinement of the structure in Pc led to differences in lengths of chemically equivalent bonds that did not seem warranted by the stereochemistry. Furthermore, the improvement in discrepancy factors (R_1 = 0.053, R_2 = 0.064) realized by this refinement was not significant, as adjudged by Hamilton's test.[8]

[8] Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

[9] The quantity minimized in the full-matrix least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, with w set at unity. Anisotropic temperature factors were applied to all 14 nonhydrogen atoms. Scattering factors were those of Cromer and Mann,[10] and the anomalous dispersion correction applied to the cobalt form factor was that of Cromer.[11]

[10] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

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[12] Bailey, W. I.; Collins, D. M.; Cotton, F. A.; Baldwin, J. C.; Kaska, W. C. *J. Organomet. Chem.* **1979**, *165*, 373. Ginsburg, R. E.; Cirjak, L. M.; Dahl, L. F. *J. Chem. Soc., Chem. Commun.* **1979**, 468. The Co-Co distance we quote is from the latter structure, which we consider to be the more reliable of the two.

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sonable for molecules containing a formal double bond between the metal atoms, as adjudged by the EAN criteria.[13] The bridging region of the μ-CH_2 compound **1** is planar, as required by the presence of a crystallographic twofold axis passing through atoms C_6, C_7, and O_6. As can be seen from Figure 1, the Co to μ-CH_2 carbon distance is longer than the Co to μ-CO carbon distance [1.909 (9) Å vs. 1.849 (8) Å]. The cobalt to μ-CH_2 carbon distance in **1** is slightly shorter than the cobalt to bridging alkylidene distances [1.951 (6) Å, 1.944 (7) Å] observed in $Co_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CH(CO_2CH_2CH_3))$;[14] this is perhaps due to the longer formal single Co–Co bond [2.495 (1) Å] in the latter compound.

Despite the intense level of interest in alkylidene ligands in organometallic chemistry during the last several years,[15] compounds containing the simplest bridging alkylidene, μ-CH_2, are still relatively rare. Single examples have been reported in binuclear Mn,[16] Rh,[17] Ru,[18] Fe,[19] and Pt[20] systems and in a trinuclear osmium cluster.[21] The binuclear cobalt compound **1** is, however, the first such example with cobalt as the metal. Furthermore, it is the only such compound with a formal double bond between the metals and with a bridging carbonyl. These unique features may play a role in the reactions of **1** with species such as CO, H_2, and alkenes.[22]

Having established the structure of **1**, we now turn to the interesting question of the source of the μ-CH_2 and μ-CO ligands. The most reasonable source appears to be the lithium enolate of acetaldehyde ($Li^+CH_2CHO^-$, LEA) generated via the reaction of THF solvent with *n*-butyllithium. This reaction has been shown to cleanly produce ethylene and LEA,[23,24] with a $t_{1/2}$ at 35 °C of 10 min.[23] Clearly, under the conditions used to prepare **1**, some enolate would have been present with the $Li^+Me_5Cp^-$ prior to addition of $CoCl_2$. In order to test this hypothesis, several reactions were carried out. First, $Li^+Me_5Cp^-$ was generated at −78 °C via the reaction of HMe_5Cp in THF with a stoichiometric amount of *n*-BuLi/hexane solution, thus avoiding the generation of LEA. After the mixture was slowly warmed to room temperature, reaction with 0.5 equiv of anhydrous $CoCl_2$ and workup were carried out as before. Only a small amount of brown solid was obtained, tentatively identified as the dichloro bridged compound $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Cl)_2$, **2**.[25] In contrast, when the reaction was carried out in a similar fashion, except for addition of 0.25 equiv of preformed LEA[26] in parallel with addition of the $CoCl_2$, the bridging methylene compound **1** was isolated in 10% yield. Similar experiments using acetaldehyde directly, instead of LEA, produced no identifiable product. Thus, the importance of LEA in the formation of **1** seems well established.

The exact mechanism by which LEA reacts with $CoCl_2$ and $Li^+Me_5Cp^-$ remains to be determined. While we assume the first step must involve metalation of the enolate, such metalations appear not to have been studied to date. This may in part be due to the difficulty of obtaining enolates of reactive aldehydes, since direct treatment of such aldehydes with base often leads to aldol condensation products. In the case of acetaldehyde, generation of the enolate via the *n*-BuLi/THF route[23,24] avoids such problems. Ready availability of LEA and the demonstration of its involvement in the formation of the novel μ-CH_2 compound **1** suggest that a general investigation of metalation of aldehyde enolates should be a fruitful venture.

Acknowledgments. Helpful discussions with J. W. Johnson and G. Doyle are gratefully acknowledged. We also wish to thank R. Pettit for informing us of his results on the binuclear iron μ-CH_2 compound prior to publication.

Supplementary Material Available: Tables of atomic positional and temperature parameters, bond distances, interatomic angles, and deviations of atoms from cyclopentadienyl least-squares planes, listings of observed and calculated structure factor amplitudes, and a diagram of the packing of molecules in the unit cell (16 pages). Ordering information is given on any current masthead page.

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(22) Very little is known at present about reactivity of μ-CH_2 ligands; recent work by Pettit and co-workers has uncovered what promises to be an interesting and potentially rich area (see ref 19). Compound **1** of our work reacts rapidly with CO, one major product being tentatively identified as $Co(\eta^5\text{-}Me_5C_5)(CO)_2$.

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(25) Crystalline **2** was prepared in moderate yield (22%) by reaction of $CoCl_2$ and Li^+Me_5Cp in a 1:1 ratio, following the same procedure. Mass spectrum, *m/e* 458 (M^+, additional peaks show appropriate pattern for two chlorines), 229 (base peak, $(Me_5Cp)CoCl$).

(26) LEA was generated in situ in THF by reaction with the appropriate amount of *n*-BuLi at room temperature for 18 h. The presence of LEA was verified by NMR (see ref 23).

$Mo_2S_4^{2+}$ Core: New Syntheses, New Complexes, and Electrochemical Diversity

Sir:

Recognition of the importance of sulfide ligation in the heterogeneous Mo catalysts used in industrial redox processes[1] and in the Mo-containing site of the enzyme nitrogenase[2] has directed increasing attention to the coordination chemistry of sulfidomolybdenum complexes. Efforts to develop mononuclear, polynuclear, and heteronuclear Mo sulfide entities which serve as structural or reactivity models for these catalytic systems have led to the synthesis of several novel Mo-[3] and Mo–Fe sulfide complexes.[4] However, progress has been significantly restricted

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