Scheme I

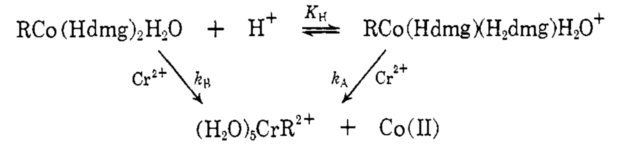

Table I. Kinetics of the Reactions of Alkylcobaloximes with Cr^{2+}_{aq} (25.0°) and Absorption Spectra of the Alkylchromium Ions

	Rate constants,[a] M^{-1} sec^{-1} k_A	k_B	Absorption spectra[b] of $(H_2O)_5CrR^{2+}$ λ_{max}, nm (ϵ, M^{-1} cm^{-1})
CH_3	23.0	14.5	530 (0.065), 392 (1.0), 258 (10.5)
CH_2CH_3	1.4×10^{-2}	1.3×10^{-2}	525 (0.037), 394 (1.0), 275 (6.1)
$CH_2CH_2CH_3$	1.38×10^{-3} [c]		522 (0.05), 394 (1.0), 275 (6.7)
$CH(CH_3)_2$	1.08×10^{-4} [c]		
$CH_2C(CH_3)_3$	6.1×10^{-5} [d]		387 (1.0),[e] 289 (4.1)
$CH_2C_6H_5$	7.3	5.0	355 (1.0), 297 (3.3), 274 (3.9), 243 (3.5)

[a] Rate constants as designated in Scheme I. [b] The spectrum is quoted relative to λ ~390 nm with values of ε, where known, as follows: CH_3 (240), C_2H_5 (166), and $CH_2C(CH_3)_3$ (204). [c] At $[H^+] \cong 0.4$ M. [d] At $[H^+] = 0.72$ M. [e] The spectrum of the neopentylchromium(III) ion is that determined by J. H. Espenson and D. A. Williams (independent observations) using an alternative synthesis.

constant, K_H.[3] Table I summarizes the values of the rate constants k_A and k_B along with the spectrum of each of the organochromium products.

The reaction appears to be applicable to methylcobalt (chelate) complexes outside the cobaloxime series; the methylchromium complex was also formed in the case of chelate = salen (k_2 = 76 M^{-1} sec^{-1}), bae (k_2 = 57 M^{-1} sec^{-1}), and Me_6 [14]-4,11-dieneN_4 ($k_2 \sim$ 4 M^{-1} sec^{-1}).[18]

In a formal sense eq 1 can be viewed as the transfer of radical R· to Cr^{2+}. We wish to consider four possible mechanisms. First, the reaction might occur by release of the radical from the original complex through homolytic scission of the Co–C σ bond, followed by capture of R· by Cr^{2+} ($R\cdot + Cr^{2+} \rightarrow CrR^{2+}$); the latter process is extremely rapid.[19] The second-order kinetics argues against this mechanism, however, as does the pronounced stability of the alkylcobaloximes toward reaction with acid,[20] and the ordering of rates for the different alkyl compounds (Table I) which does not at all follow the order expected for a homolytic scission reaction forming alkyl radicals.

Second, one can envisage a Cr(II) catalysis of this homolysis which accounts for the form of the rate expression but to which the other objections apply (as well as the inherent chemical unreasonableness of Cr(II) catalysis of such a dissociation).

Third, we consider a concerted process in which the transfer of a carbanion from cobalt to chromium accompanies electron transfer from chromium to cobalt. Fourth, we consider a process rarely if ever encountered in organic reactions,[21] involving bimolecular homolytic substitution at saturated carbon (S_H2 mechanism). These latter mechanisms both appear to be in accord with the data at hand. Based upon the marked decrease in rate with substitution at the α carbon, it is tempting to suggest that the reaction occurs with inversion of configuration at carbon.

Additional experiments are in progress to define the mechanism more completely, and to resolve the question of the stereochemical change at the α carbon atom.

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[18] T. S. Roche and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 8622 (1972), indicated that the products of reaction of this methyl complex with Cr^{2+} were $Cr(H_2O)_6{}^{3+}$ and CH_4, but their studies were made at 1 M H^+ where the acid hydrolysis of $CrCH_3{}^{2+}$ occurs relatively rapidly.

[19] H. Cohen and D. Meyerstein, *J. Chem. Soc.*, *Chem. Commun.*, 320 (1972).

[20] Were the alkylcobaloximes subject to thermal homolysis, $R(Co) \rightleftharpoons R\cdot + (Co^{II})$, as is the case photochemically [G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *J. Amer. Chem. Soc.*, **92**, 2997 (1970)], acidic solutions would be quite unstable, which is not the case. This conclusion is not altered by postulating a high recombination rate between R· and (Co^{II}), provided the latter are free entities whose reaction rate cannot exceed the limit of diffusion control, because the decomposition of the Co(II) compound by perchloric acid is exceedingly rapid: A. Adin and J. H. Espenson, *Inorg. Chem.*, **11**, 686 (1972).

[21] K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971, pp 72–90.

Synthesis, Stereochemistry, and Bonding of Tetrapyridinemagnesium(II) Bis(π-cyclopentadienyltricarbonylmolybdate(–I)) and Related Compounds

Sir:

It was suggested in a recent communication[1] that direct magnesium–transition metal bonding occurs quite generally in a broad class of "mixed metal" complexes. While such metal–metal bonds might well exist in selected cases, results from this laboratory provide an alternative bonding pattern for these bimetallic complexes.[2] We describe herein the preparation and spectroscopic properties of a series of complexes with the general formula $m_2Mg(py)_4$ (m = metal carbonyl group; py = pyridine) and the crystal and molecular structure of one of these, $Mg[h^5\text{-}C_5H_5Mo(CO)_3]_2(C_5H_5N)_4$ (**1**).

By analogy with the mMgX (X = Cl, Br) systems[2,3] complex **1** was prepared by a metal exchange reaction of magnesium and the corresponding m_2Hg derivative in tetrahydrofuran (THF). The highly insoluble THF complex that initially precipitated was converted to **1** by recrystallization from pyridine.[4,5] The other com-

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[1] G. B. McVicker and R. S. Matyas, *J. Chem. Soc.*, *Chem. Commun.*, 972 (1972).

[2] S. W. Ulmer, Ph.D. Thesis, Cornell University, 1972.

[3] J. M. Burlitch and S. W. Ulmer, *J. Organometal. Chem.*, **19**, P21 (1969).

[4] Stirring a THF solution (25 ml) of $Hg[Mo(CO)_3C_5H_5]_2$ (1 mmol) with magnesium (10 mg-atoms, 80 mesh) for 8 hr at 25° under argon produced a light green solid which was collected, dried under vacuum, and recrystallized from boiling, dry, deaerated pyridine (15–20 ml). Extremely air-sensitive, yellow crystals of **1** were obtained in 65% yield. Alternatively **1** may be prepared by directly carrying out the exchange reaction in pyridine or in a solution of pyridine and toluene.[5] *Anal.* Calcd: C, 52.00; H, 3.61; N, 6.75. Found: C, 52.14; H, 3.57; N, 6.49.

[5] J. M. Burlitch and R. C. Winterton, unpublished observations.

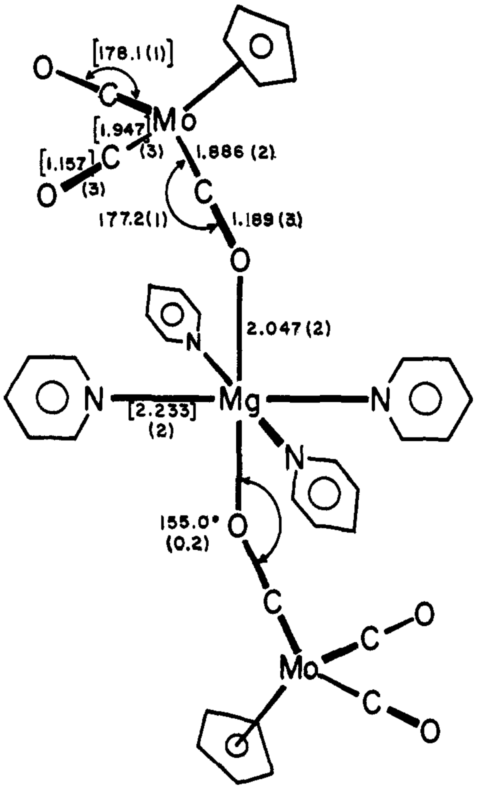

Figure 1. A portion of the structure of $[h^5\text{-}C_5H_5Mo(CO)_3]_2Mg(C_5H_5N)_4$. Average values of bond lengths (Å) or bond angles (deg) are enclosed in brackets.

pounds in the series (**2**, **3**, and **4** in Table I) were prepared from excess magnesium amalgam[6] and either the appropriate m_2Hg derivative (method A) or the dimeric metal carbonyl (method B) in toluene containing a small excess of pyridine. All of the compounds were isolated in yields of 45–70% as air- and moisture-sensitive crystalline solids; all had C, H, and N analyses in good agreement with the indicated compositions.

The structure of **1** was determined from a single-crystal X-ray diffraction analysis of 6186 diffractometer-recorded reflections.[7] Block-diagonal refinement of the coordinates and anisotropic thermal parameters of 25 independent nonhydrogen atoms yielded a final weighted residual, R_w, of 0.042. The structure (Figure 1) consists of centrosymmetric molecules, which exhibit octahedral coordination of magnesium by four normal pyridine ligands, and two trans *pentahapto*cyclopentadienyltricarbonylmolybdenum groups. The latter display the same bonding pattern found in the analogous tungsten-containing groups in $(THF)_3Al[OCW(CO)_2C_5H_5]_3$[8] (**5**). Of particular interest is the direct linkage of the magnesium atom to a carbonyl oxygen atom; this is the first definitive example of O-coordination of a carbonyl ligand to a main-group metal other than aluminum.[9]

Table I. Infrared Spectra of $m_2Mg(py)_4$ Compounds

No.	m	Carbonyl absorptions, cm^{-1}
1	$C_5H_5Mo(CO)_3$[a]	1915 (s), 1819 (s), 1664 (s)[c] 1918 (s), 1828 (s), 1667 (s)[d]
2	$C_5H_5Fe(CO)_2$[b]	1875 (s), 1773 (w), 1711 (s)[c]
3	$Co(CO)_4$[a]	2024 (m), 1935 (s), 1930 (sh), 1751 (s)[e]
4	$Mn(CO)_5$[b]	2031 (w), 1928 (s), 1904 (s), 1721 (s)[e]

[a] Prepared by method A (see text). [b] Prepared by method B. [c] Pyridine solution. [d] Nujol mull. [e] Toluene solution.

Some important bond distances and angles are shown in Figure 1. The Mg–O bond length is 2.047 (2) Å; the analogous Al–O bond length in **5** is 1.827 (9) Å. The oxygen–magnesium coordination perturbs the adjoining C–O bond much less than does the oxygen–aluminum coordination. The C–O distance in **1** is 1.189 (3) Å and the corresponding distance in **5** is 1.25 (2) Å; these values are significantly larger than the mean length of 1.157 (3) Å found in the terminal carbonyls of **1**. As was observed for **5**,[8] this perturbation is reflected in the infrared spectrum (Table I). The 1667 cm^{-1} absorption is assigned to the asymmetric mode of the doubly coordinated carbonyls and the absorptions at 1918 and 1828 cm^{-1} to the terminal carbonyls. The spectra of the complexes **2**, **3**, and **4** contain features similar to those of **1** and may be analyzed in the same fashion.

A comparison of this spectrum with that of $Na^+Mo(CO)_3C_5H_5^-$ (ν_{CO} at 1893 (s), 1775 (s), and 1749 (m, sh) cm^{-1} in pyridine)[2] reveals that the formation of the magnesium-to-oxygen bond is associated with a decrease of 82 cm^{-1} in the lowest frequency carbonyl absorption. In fact, both in solution *and* in the solid state, similar shifts of 60–90 cm^{-1} occur for all $m_2Mg(py)_4$ compounds studied. Nevertheless in each case the average carbonyl frequency is essentially unchanged by oxygen coordination. Moreover, the coordination geometry of the $C_5H_5Mo(CO)_3$ group is very similar to that of $C_5H_5Mn(CO)_3$[10] which, in turn, is isoelectronic with $C_5H_5Cr(CO)_3^-$. Thus it appears that the inherent ionic character of the metal carbonyl group is not seriously perturbed by the formation of a strong coordinate–covalent bond through a carbonyl oxygen.

In support of this view we note that the metal carbonyl moiety retains substantial nucleophilic character and is highly reactive, even in nonpolar solvents. Useful synthetic applications result from the solubility of some of these derivatives (particularly **3** and **4**) in aromatic hydrocarbons in which magnesium halide is insoluble. A noteworthy example is the conversion of $(C_6H_5)_3SiCl$, *via* **4** in toluene, to $(C_6H_5)_3SiMn(CO)_5$ in

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(6) Magnesium amalgam was prepared by treatment of the metal with a THF solution of mercuric chloride. In the case of **2** at least, the presence of a trace of magnesium chloride was necessary to promote the reaction with the metal carbonyl dimer. The typical procedure for all reactions (1 mmol scale) employing magnesium amalgam was to stir 10 mg-atoms of 80 mesh magnesium in 15 ml of dry, deaerated THF containing 2 mmol of mercury(II) chloride. After several minutes the solvent was removed with a syringe, and the gray residue was washed with three 15-ml portions of THF, then dried under vacuum.

(7) A 0.7 × 0.4 × 0.2 mm crystal of **1**, sealed in a thin-walled capillary under argon, displayed triclinic X-ray diffraction symmetry with $a = 8.505 \pm 0.002$, $b = 11.073 \pm 0.002$, $c = 11.034 \pm 0.002$ Å; $\alpha = 117.88 \pm 0.01$, $\beta = 108.26 \pm 0.01$, $\gamma = 90.34 \pm 0.01°$; and $\rho_{obsd} = 1.6$ g cm^{-3}, $\rho_{calcd} = 1.6$ g cm^{-3} for $Z = 1$ in $P\bar{1}$. Of 7549 reflections investigated in the range $0 < \sin\theta/\lambda \leq 0.805$ Å^{-1}, 6186 were statistically acceptable as observed data. The block-diagonal least-squares refinement converged with a final weighted residual $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$, where $w = 1/(\sigma_F)^2$, and a data-parameter ratio of 27.4:1. The conventional R is 0.051.

(8) R. B. Petersen, J. J. Stezowski, Che'ng Wan, J. M. Burlitch, and R. E. Hughes, *J. Amer. Chem. Soc.*, 93, 3532 (1971).

(9) D. F. Shriver, *Chem. Brit.*, 8, 419 (1972).

(10) A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, 16, 118 (1963).

34% yield;[2] the latter is inaccessible using $Na^+Mn(CO)_5^-$ in THF.[11,12]

[11] M. D. Curtis, *Inorg. Chem.*, **11**, 802 (1972).

[12] This work was supported by the National Science Foundation, the Alfred P. Sloan Foundation, and the Materials Science Center of Cornell University. We thank the Climax Molybdenum Co., a Division of American Metal Climax, Inc., for gifts of chemicals.

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Triplet State of Ketones in Solutions. Quenching Rate Studies of Thioxanthenone Triplets by Flash Absorption[1]

Sir:

The quenching of the triplet $\pi\pi^*$ state of aromatic ketones by the ground-state ketones (self-quenching) has been of interest in studies of triplet sensitization of photochemical reactions, especially because of the possible intervention of a triplet exciplex in the quenching process.[2,3] Chapman and Wampfler[2] first reported the interesting observation that triplet thioxanthenone underwent a self-quenching process. A self-quenching rate constant (k_{sq}) of 6×10^{10} M^{-1} sec^{-1} in $(CH_3)_3COH$ was obtained, based on thioxanthenone sensitization studies of 4,4-dimethyl-2-cyclohexenone and assuming that triplet energy transfer was diffusion controlled. Recently, the k_{sq} for thioxanthenone was redetermined by DeBoer and Schlessinger[3] (using *trans*-stilbene as a triplet quencher) and was found to be $(2.3 \pm 0.5) \times 10^9$ M^{-1} sec^{-1} in benzene. The latter authors pointed out that energy transfer from triplet thioxanthenone (E_T = 65 kcal mol^{-1}) to the enone (E_T = 70 kcal mol^{-1}) should be considerably less than diffusion controlled. Based on known triplet energy transfer data,[4] the k_q for processes which are endothermic by 5 kcal mol^{-1} can be predicted to be two or three orders of magnitude less than those of the diffusion controlled or to be $\sim 1 \times 10^7$ M^{-1} sec^{-1} in this case. Taking this lower value for enone quenching of triplet thioxanthenone, and the data of Chapman and Wampfler,[2] a k_{sq} $\sim 2 \times 10^8$ M^{-1} sec^{-1} in $(CH_3)_3COH$ can be calculated. This recalculated value for k_{sq} is ten times lower than the recently reported value in benzene[3] and could imply a large solvent effect, a genuine inconsistency, or some other factor such as differences in purity of the thioxanthenone.

A transient absorption at λ_{max} 625 ± 5 nm was observed when a degassed solution of 5×10^{-4} M thioxanthenone[5] in acetonitrile (620 ± 5 nm in $(CH_3)_3COH$) was flash photolyzed.[6] Monitoring at 600 nm, the transient lifetime was observed to decrease as the concentration of thioxanthenone was increased from 1×10^{-4} to 5×10^{-3} M in acetonitrile. From a plot of k_{obsd} ($= 1/\tau$) against concentration of thioxanthenone, we obtained τ = 73 μsec from the intercept and k_{sq} = $(2.3 \pm 0.1) \times 10^7$ M^{-1} sec^{-1} from the slope. The lifetime is in good agreement with the lifetime of triplet thioxanthenone of 77 μsec reported earlier by Herkstroeter and Hammond.[4b] To obtain further data on the transient, we measured the k_q in acetonitrile for several quenchers with different triplet energies (Table I). In confirmation with Hammond's assignment of the transient to the triplet excited state of thioxanthenone we observed diffusion-controlled quenching for quenchers with E_T lower than that of thioxanthenone (E_T 65 kcal mol^{-1} [7]) and found a sharp break in rate constants as the triplet energy of the quencher exceeded that of thioxanthenone.

Table I. Rate Constant for Quenching of Triplet Thioxanthenone

Quencher	E_T, kcal mol^{-1}	Solvent	k_q, M^{-1} sec^{-1}
Thioxanthenone[a]	65[f]	Acetonitrile	$(2.3 \pm 0.1) \times 10^7$
		Benzene	$(1.8 \pm 0.1) \times 10^6$
		$(CH_3)_3COH$	$(8.4 \pm 0.5) \times 10^6$
Thioxanthenone[b]		Acetonitrile	$(4.9 \pm 0.1) \times 10^7$
Thioxanthenone		$(CH_3)_3COH$	1.4×10^8 [c]
Thioxanthenone		Benzene	$(2.3 \pm 0.5) \times 10^9$ [d]
4,4-Dimethyl-2-cyclohexenone	70[g]	Acetonitrile	$(2.5 \pm 0.1) \times 10^7$
		$(CH_3)_3COH$	$(8.6 \pm 0.7) \times 10^6$
Dibenzothiophene		Acetonitrile	7.8×10^5
Fluorene	68[h]	Acetonitrile	$(2.2 \pm 0.1) \times 10^8$
Naphthalene	61[h]	Acetonitrile	$(1.3 \pm 0.1) \times 10^{10}$
trans-1,3-Pentadiene	59[i]	Acetonitrile	$(8.2 \pm 0.5) \times 10^9$ [e]
		$(CH_3)_3COH$	$(1.2 \pm 0.1) \times 10^9$ [e]
trans-Stilbene	50[j]	Acetonitrile	$(2.6 \pm 0.1) \times 10^{10}$

[a] Obtained from Baker Chemical Co. and purified according to ref 4. [b] Unpurified sample from Baker Chemical Co. We were unable to observe any transient from an unpurified sample from Aldrich Chemical Co. in the concentration range used with the Baker purified and unpurified samples. [c] Recalculated value using our measured k_q for the enone and the data of ref 2. [d] Reference 3. [e] S. K. Dogra, unpublished results. [f] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298. [g] Reference 8. [h] Reference 7. [i] R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965). [j] Reference 4b.

Quenching and self-quenching measurements were determined in $(CH_3)_3COH$, benzene, and acetonitrile (Table I). Included among the quenchers were 4,4-dimethyl-2-cyclohexenone, *trans*-1,3-pentadiene, and dibenzothiophene. Our value of k_q = 8.6×10^6 M^{-1} sec^{-1} for quenching by the enone in $(CH_3)_3COH$ agrees with de Mayo's estimate of 70 kcal mol^{-1} for the triplet energy of the enone chromophone.[8] Taking our directly measured value for triplet quenching by 4,4-dimethyl-2-cyclohexenone in $(CH_3)_3COH$, we can recalculate a k_{sq} of 1.4×10^8 M^{-1} sec^{-1} for thioxanthenone from the results reported by Chapman.[2] This is over ten times higher than our measured k_{sq} of 8.4×10^6 M^{-1} sec^{-1} in the same solvent but is lower than the revised value of 2.3×10^9 M^{-1} sec^{-1} (in benzene) recently reported by DeBoer and Schlessinger.[3] Our directly measured value of k_{sq} in benzene

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[1] Issued as National Research Council of Canada Contribution No. 13327.

[2] O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969).

[3] C. D. DeBoer and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **94**, 655 (1972).

[4] (a) K. Sandros and H. L. J. Backstrom, *Acta Chem. Scand.*, **16**, 958 (1962); (b) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966); (c) R. W. Yip, W. D. Riddell, and A. G. Szabo, *Can. J. Chem.*, **48**, 987 (1970).

[5] Purified by recrystallization from ethanol three times and then sublimed twice, mp 209–210°.

[6] The degassing procedure and apparatus were as previously described: R. W. Yip, W. D. Riddell, and A. G. Szabo, *Can. J. Chem.*, **48**, 987 (1970).

[7] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

[8] P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971).