

- (7) The air sensitivity of the substance precluded a quantitative determination of extinction coefficients at this preliminary stage.
 (8) A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *Chem. Commun.*, 1133 (1970).
 (9) As expected, each component of this doublet appears as a finely split doublet of triplets.
 (10) Chemical shifts denote the *upfield* displacement (in ppm) of each resonance from that of the accepted standard, trichlorofluoromethane.
 (11) NDEA Graduate Fellow, 1971-1974.
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Synthesis and Structure of the Pentacarbonylmetalate Dianions of Chromium, Molybdenum, and Tungsten

Sir:

Systematic studies on the chemistry of the pentacarbonylmetalate dianions of Cr, Mo, and W have been hampered by the lack of facile syntheses.¹⁻⁵ Our desire to determine whether these dianions will be useful as stoichiometric reagents in organic syntheses and/or precursors to novel organotransition metal complexes has prompted us to examine new routes to these species. In this process general methods for the synthesis of these monomeric dianions have been discovered: the alkali metal reduction of $M(\text{CO})_6$, $M(\text{CO})_5(\text{halide})^-$, or $M_2(\text{CO})_{10}^{2-}$ in hexamethylphosphoramide (HMPA).

In 1968 it was reported that $\text{Cr}(\text{CO})_6$ was reduced by sodium metal in HMPA to give a substance formulated as " $\text{Cr}(\text{CO})_5\text{HMPA}^{2-}$ " on the basis of infrared spectra and sodium metal uptake.⁶ Under the same conditions as reported in this paper,⁶ we have obtained entirely different infrared spectra of the reduced chromium species in HMPA by using air-tight sodium chloride solution cells. Virtually identical spectra have also been obtained from analogous reductions of $M(\text{CO})_6$ ($M = \text{Mo}, \text{W}$), $M'_2(\text{CO})_{10}^{2-}$ ($M' = \text{Cr}, \text{Mo}, \text{W}$), and $M'(\text{CO})_5\text{X}^-$ ($X = \text{Cl}, \text{Br}, \text{I}$) in HMPA. Figure 1 shows various stages in the reduction of $\text{W}(\text{CO})_6$ in HMPA at room temperature. The principal intermediate in this reduction is $\text{W}_2(\text{CO})_{10}^{2-}$ which absorbs at 1939 (m), 1889 (vs), and 1790 cm^{-1} (s) in the carbonyl region. After approximately 4 hr all bands due to $\text{W}_2(\text{CO})_{10}^{2-}$ disappear; only bands at 1775 (vs) and 1731 cm^{-1} (vs) remain, which are attributed to $\text{Na}_2\text{W}(\text{CO})_5$.

Proof that the reduced chromium substance obtained in HMPA is identical with genuine $\text{Na}_2\text{Cr}(\text{CO})_5$, prepared by Behrens's method,² was provided by showing that HMPA solution spectra of substances made by both methods are identical. Further, by exposing HMPA solutions of $\text{Na}_2\text{Cr}(\text{CO})_5$ to air, spectra have been obtained which are virtually identical with that attributed to " $\text{Cr}(\text{CO})_5\text{HMPA}^{2-}$."⁷ Since we have shown that trace amounts of oxygen instantaneously convert $\text{Cr}(\text{CO})_5^{2-}$ to $\text{Cr}_2(\text{CO})_{10}^{2-}$, we believe that the species previously reported as " $\text{Cr}(\text{CO})_5\text{HMPA}^{2-}$ " is, in fact, mostly $\text{Cr}_2(\text{CO})_{10}^{2-}$.

Infrared spectra of $\text{Na}_2M(\text{CO})_5$ ($M = \text{Cr}, \text{Mo}$ and W) in HMPA (see Table I) show only two strong infrared active bands below 1800 cm^{-1} as expected for trigonal bipyramidal dianionic carbonyl species. Thus, little or no coordination of $M(\text{CO})_5^{2-}$ with the HMPA is indicated.⁸⁻¹⁰ Our spectra of $\text{Na}_2\text{Cr}(\text{CO})_5$ in tetrahydrofuran (THF) are in agreement with that reported recently by Behrens, *et al.*² Marked differences in the spectra of $\text{Na}_2\text{Cr}(\text{CO})_5$ in HMPA and THF are undoubtedly due to substantial ion pair formation in the latter solvent which effectively reduc-

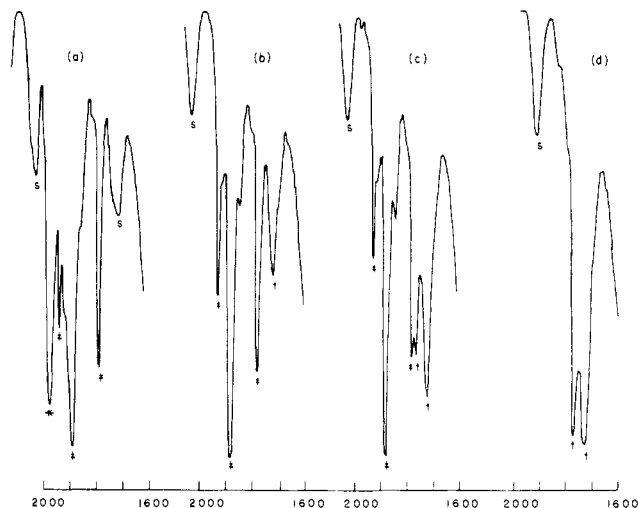


Figure 1. Infrared spectra showing the reduction of $\text{W}(\text{CO})_6$ by Na in HMPA at various times: (a) 1 hr, (b) 2.5 hr, (c) 3 hr, (d) 4 hr. Identity and positions of bands: s = HMPA; * = $\text{W}(\text{CO})_6$, 1973 cm^{-1} ; ‡ = $\text{W}_2(\text{CO})_{10}^{2-}$, 1938, 1889, 1789 cm^{-1} ; † = $\text{W}(\text{CO})_5^{2-}$, 1775, 1731 cm^{-1} .

Table I. Infrared Solution Spectra of Salts of $M(\text{CO})_5^{2-}$ in Carbonyl Stretching Frequency Region

Salt	Solvent	Carbonyl stretching frequencies (cm^{-1})
$\text{Na}_2\text{Cr}(\text{CO})_5$	HMPA	1760 (s), 1722 (s)
$\text{Na}_2\text{Cr}(\text{CO})_5$	THF	1819 (s), 1768 (s, br) ¹¹
$\text{Na}_2\text{Mo}(\text{CO})_5$	HMPA	1769 (s), 1723 (s)
$\text{Na}_2\text{W}(\text{CO})_5$	HMPA	1775 (s), 1731 (s)

es the symmetry of $\text{Cr}(\text{CO})_5^{2-}$ from D_{3h} in HMPA to approximately C_{4v} in THF.¹²⁻¹⁴ However, in contrast to their report that $\text{Cr}(\text{CO})_5^{2-}$ decomposes almost entirely to $\text{Cr}_2(\text{CO})_{10}^{2-}$ within 95 min in THF,² we find virtually no change in the spectra of THF solutions of $\text{Na}_2\text{Cr}(\text{CO})_5$ maintained under an atmosphere of moisture- and oxygen-free nitrogen for at least seven days.¹⁵ As mentioned previously, trace amounts of air instantaneously convert $\text{Cr}(\text{CO})_5^{2-}$ to $\text{Cr}_2(\text{CO})_{10}^{2-}$; the latter is characterized by a strong absorption in THF at 1890 cm^{-1} .¹⁶

The chemical properties of the pentacarbonylmetalate dianions are under study. They react with a variety of main-group and transition metal halides to generate products of the general formula $M(\text{CO})_5\text{E}^-$ by simple halide displacement. An account of this chemistry will be published in the near future.

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References and Notes

- Approximately 95% yields of $\text{Na}_2\text{Cr}(\text{CO})_5$ have been obtained by Na reduction of $\text{Cr}(\text{CO})_6$ in ammonia.² However, analogous reductions of molybdenum and tungsten hexacarbonyls provide only poor yields of the monomeric dianions, contaminated with other salts.³ Small quantities of pure $\text{Na}_2M(\text{CO})_5$ ($M = \text{Mo}, \text{W}$) are obtained by the disproportionation of $\text{Na}_2M_2(\text{CO})_{10}$ above 130° under a carbon monoxide atmosphere in a sealed tube. The latter is a technically difficult synthesis, useful for preparing only small amounts of the dianions.^{4,5}
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- (7) See Figures 2 and 3 in ref 6.
 (8) Infrared spectra of isoelectronic D_{3h} $M(\text{CO})_5^-$ ($M = \text{Mn, Tc, Re}$) and $\text{Fe}(\text{CO})_5$ show E' and A_2'' modes at substantially higher energy. Sodium salts of $M(\text{CO})_5^-$ in tetrahydrofuran absorb at 1898 (s), 1864 (s) ($M = \text{Mn}$), 1911 (s) and 1865 (s) ($M = \text{Tc}$) and 1910 (s) and 1864 (s) ($M = \text{Re}$).⁹ Neutral $\text{Fe}(\text{CO})_5$ in Nujol absorbs at 2024 (s) and 1984 (s).¹⁰ All values are in cm^{-1} .
 (9) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).
 (10) H. P. Fritz and E. P. Paulus, *Z. Naturforsch. B*, **18**, 437 (1963).
 (11) Reported previously² as 1820 (s), 1772 (s), and 1738 (s cm^{-1}).
 (12) While $\text{Na}_2\text{Cr}(\text{CO})_5$ shows sharp bands at 1760 and 1722 cm^{-1} in HMPA, it exhibits a sharp band at considerably higher frequency, 1819 cm^{-1} , and a broad absorption at ca. 1768 cm^{-1} in THF. Behrens, *et al.*,² suggest that the latter absorption consists of two bands (1772, 1738 cm^{-1}) and on this basis assign a symmetry of C_{4v} to $\text{Cr}(\text{CO})_5^{2-}$ in THF. Edgell has established that ion pair formation in THF can effectively lower the symmetry of carbonylmetalate ions; e.g., that of $\text{Co}(\text{CO})_4^-$ (counterion Na^+) is lowered from T_d to C_{3v} in THF.¹³ It appears likely that $\text{Na}_2\text{Cr}(\text{CO})_5$ exists in THF as tight ion pairs in view of Collman's evidence that constitutionally similar $\text{Na}_2\text{Fe}(\text{CO})_4$ forms such ionic aggregates in this solvent. In contrast, ion pair formation in HMPA is relatively unimportant for $\text{Na}_2\text{Fe}(\text{CO})_4$ ¹⁴ and, by inference, for $\text{Na}_2\text{Cr}(\text{CO})_5$.
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 (14) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Amer. Chem. Soc.*, **94**, 5905 (1972).
 (15) Solutions of THF prepared and stored in stoppered flask in Vacuum Atmospheres Co. glove box.
 (16) R. G. Hayter, *J. Amer. Chem. Soc.*, **88**, 4376 (1966).

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Carbon Monoxide and Methyl Groups as Symbiotic Trans Ligands in an Iron(II) Complex, $[\text{Fe}(\text{C}_{10}\text{H}_{19}\text{N}_8)(\text{CO})(\text{CH}_3)]$

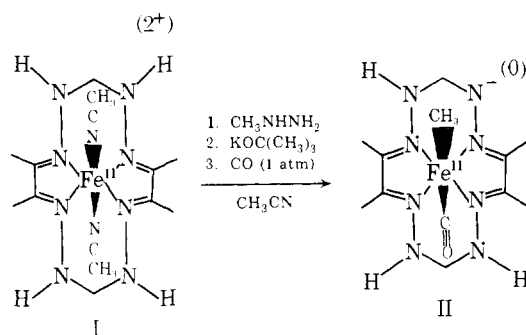
Sir:

The synthetic non-porphyrin macrocyclic complexes of iron have recently been shown to have a very diverse chemistry which complements the naturally occurring iron heme systems. Redox reactions have been observed in which iron assists in the oxidation of the planar macrocyclic ligand,¹ iron(III) alkyls have been formed by the oxidative deamination of alkyl hydrazines,² a number of iron(II) complexes have been shown to reversibly bind carbon monoxide,^{3,4} and iron(I) complexes, including iron(I) hydrides, have been characterized.⁵

This report describes the preparation and structural characterization of a macrocyclic iron(II) complex which contains carbon monoxide and a methyl group in the axial positions. The results of this structural characterization are relevant to the study of the interaction of carbon monoxide with the isoelectronic cobalt(III)-alkyl complexes.⁶ There has been intense interest in the reductive Co-C bond cleavage of alkylcorrins and other vitamin B₁₂ model compounds by carbon monoxide.⁷ Evidence has been obtained for the existence of 1:1 carbon monoxide complexes of methylcobaloxime in solution,⁸ but we are unaware of any successful attempts in which carbon monoxide adducts of cobalt(III)-alkyl complexes have been isolated. However, the analogous complexes of iron(II) should be more stable for the following reasons. First, low spin iron(II) forms stronger carbon monoxide complexes because it has better π -donor properties than cobalt(III). Stable carbon monoxide complexes of synthetic macrocyclic complexes of iron(II) have been well characterized.^{3,4} Secondly, although iron(II)-alkyl complexes of tetraaza ligands are rare, alkyl complexes of bis- α, α' -dipyridyliron(II) are known.⁹ Macrocyclic ligands containing α -diimine functions, such as I, might also stabilize iron(II)-alkyl bonds. Thirdly, a symbiotic relationship may exist between the bonding of carbon monoxide and alkyl groups whose trans effects are composed of

contrasting interactions, *i.e.*, the strong π -acceptor properties of carbon monoxide vs. the strong σ -donor properties of alkyl groups.

The reaction of the bis- α -diimineiron(II) complex, I,¹⁰ with carbon monoxide and CH_3NHNH_2 in trifluoroethanol results in the formation of a complex, $[\text{Fe}(\text{C}_{10}\text{H}_{20}\text{N}_8)(\text{CO})(\text{CH}_3\text{NHNH}_2)]^{2+}$, containing weakly bound carbon monoxide ($\nu = 2035 \text{ cm}^{-1}$). Dissolution of the complex in acetonitrile results in rapid loss of CO. However, if the complex is dissolved in acetonitrile under 1 atm of CO pressure, followed by the addition of potassium *tert*-butoxide with a slight excess of methylhydrazine, a complicated series of reactions takes place. The strongly basic alkoxide deprotonates the ligand. It may also result in some disproportionation of the iron to the univalent and trivalent states in a manner similar to that established for the disproportionation of cobaloximes under basic conditions.¹¹ Oxidative deamination of CH_3NHNH_2 also occurs with the methyl group being transferred to iron, as observed for some other cobalt and iron complexes,² yielding the desired complex, $[\text{Fe}(\text{C}_{10}\text{H}_{19}\text{N}_8)(\text{CO})(\text{CH}_3)]$ (II).¹²



The compound is stable in wet or dry DMSO solutions for weeks when under a carbon monoxide atmosphere. It is not noticeably light sensitive, but does decompose rapidly when exposed to molecular oxygen. The carbon monoxide binding, which competes with the strong π -acceptor properties of the α -diimine functions of the macrocyclic ligand, is strengthened by the increased electron density placed on the iron by the methyl group. The carbon monoxide stretching frequency in $[\text{Fe}(\text{C}_{10}\text{H}_{19}\text{N}_8)(\text{CO})(\text{CH}_3)]$ ($\nu = 1925 \text{ cm}^{-1}$) is about 100 cm^{-1} lower than with CO complexes of iron(II) complexes with α -diimine ligands of I and the complexes described by Rose, *et al.*³ The carbon monoxide in turn provides the iron(II) with an electronic environment conducive to forming a stable bond with the strong σ -donor properties of CH_3^- . The nmr spectrum (δ ; solvent, $\text{DMSO}-d_6$; Fe- CH_3 , 0.15 ppm; ligand CH_3 's, 2.05 and 2.20 ppm; ligand CH_2 's, 4.3 and 3.85 ppm) is similar to that expected for analogous Co(III) CH_3 complexes. The compound reacts with strong acids to give CH_4 and with Hg^{2+} in $\text{DMSO}-d_6$ immediately (on mixing) to produce CH_3Hg^+ (nmr, 0.9 ppm).

The crystal structure of this complex was determined to examine the nature of the bonding of the coordination sphere and to establish whether the dominating trans effect is produced by the methyl group or carbon monoxide.

Crystals of the compound were found to belong to the space group $Cmcm$: $a = 8.237$ (2), $b = 13.929$ (4), $c = 13.418$ (4) Å; $\rho_{\text{calcd}} = 1.51$, $\rho_{\text{expl}} = 1.49 \text{ g cm}^{-3}$ for which $Z = 4$. A total of 1093 reflections were measured to $\sin \theta/\lambda = 0.6497$ on a Picker-FACS-1 diffractometer with Mo $K\alpha$ radiation. The structure was solved by the heavy atom method and refined by conventional full-matrix least squares and Fourier techniques. Refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms converged to a final $R = 4.2\%$ ($R_w = 3.4\%$) with 872 data with