tadiene and trimethylenemethane are similar.

However, the fact that the weighted average of the C 1s binding energies of the trimethylenemethane ligand is actually slightly less than the C 1s binding energy of the butadiene ligand suggests slightly greater back-bonding to trimethylenemethane than to butadiene. This interpretation is consistent with the fact that the Fe $2p_{3/2}$, carbonyl C 1s, and O 1s binding energies are higher (by 0.30, 0.14, and 0.07 eV, respectively) in the trimethylenemethane complex than in the butadiene complex. Indeed, even infrared C–O stretching frequencies indicate more back-bonding to the trimethyleneemethane ligand than to the butadiene ligand.[22]

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE73-05133 A02) and the U.S. Energy Research and Development Administration. We wish to thank Mr. Tom Webb for preparation of butadieneiron tricarbonyl.

Registry No. $(CH_2)_3CFe(CO)_3$, 12078-33-0; $(C_4H_6)Fe(CO)_3$, 12078-32-9.

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Trans Group 6 Metal Dicarbonyls. Stereochemical Control by Seven-Coordinate Intermediates

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Associative substitution reactions of four-coordinate species which proceed stereospecifically because of the nature of the five-coordinate intermediate or transition state are well established.[1] Several examples of similar stereochemical control in dissociative substitution reactions of octahedral species are also available.[2] In principle, the geometric and site preferences of a seven-coordinate intermediate or transition state should be capable of determining the overall stereochemistry of associative substitution reactions. However, no such examples are explicitly known.

The group 6 dicarbonyls of the general formula $M(CO)_2(L\text{-}L)_2$ (L-L = bidentate phosphine or arsine) generally exist as the thermodynamically favored cis isomers,[3] with the exception of the chromium complexes $Cr(CO)_2[o\text{-}C_6H_4(PEt_2)_2]_2$ and $Cr(CO)_2[C_2H_4(PPh_2)_2]_2$, which exhibit cis–trans isomerism.[4] In contrast, the analogous seven-coordinate hydrides, $[MH(CO)_2(L\text{-}L)_2]^+$, possess a monocapped octahedral structure, in which the carbonyls are mutually trans.[5,6] We report a simple preparation of metastable *trans*-$M(CO)_2(L\text{-}L)_2$ utilizing the stereochemistry of the seven-coordinate hydride as a controlling factor.

Experimental Section

Solvents were purified by distillation from sodium benzophenone ketyl except for *tert*-butyl alcohol, which was distilled from sodium. *cis*-$Mo(CO)_2(dmpe)_2$,[5a,7] *cis*-$Mo(CO)_2(diphos)_2$,[3] *cis*-$Mo(CO)_2(diars)_2$,[8] and *cis*-$W(CO)_2(dmpe)_2$[5a] were prepared by literature methods.[9]

All reactions were performed under an atmosphere of prepurified nitrogen. Infrared, 100-MHz ^1H and 40.5-MHz ^{31}P NMR, and mass spectra were obtained on Perkin-Elmer 457A, Varian XL-100, and AEI MS-9 spectrometers, respectively. ^{31}P NMR chemical shifts are relative to external 85% phosphoric acid. Elemental analyses were by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

$[MoH(CO)_2(diphos)_2][SO_3F]$ (1). HSO_3F (39 μL, 0.68 mmol) was added via a syringe to 450 mg (0.47 mmol) of *cis*-$Mo(CO)_2(diphos)_2$ in 25 mL of tetrahydrofuran. The extent of the reaction was monitored by infrared spectroscopy and within minutes complete conversion to the hydride was achieved. The solvent was removed in vacuo leaving light pink crystals. Recrystallization from tetrahydrofuran afforded 400 mg of **1**: ^1H NMR (acetone-d_6) τ 15.28 (triplet of triplets, J_{P_AH} = 70.8, J_{P_BH} = 14.0 Hz); $^{31}P\{^1H\}$ NMR (acetone) 26.1 and 49.0 ppm (AA′BB′ pattern); IR (THF solution) ν_{CO} 1873 cm^{-1} (vs).

Anal. Calcd for $C_{54}H_{49}FMoO_5P_4S$: C, 61.84; H, 4.71. Found: C, 62.08; H, 4.87.

$[MoH(CO)_2(dmpe)_2][SO_3F]$ (2). **2** was prepared analogously except that ether was used as the solvent: ^1H NMR (Me_2SO-d_6) τ 16.20 (triplet of triplets, J_{P_AH} = 68.2, J_{P_BH} = 8.6 Hz); $^{31}P\{^1H\}$ NMR (acetone) 28.9 and 51.9 ppm (AA′BB′ pattern); IR (THF solution) ν_{CO} 1868 cm^{-1} (vs).

Anal. Calcd for $C_{14}H_{33}FMoO_5P_4S$: C, 30.45; H, 6.02. Found: C, 29.93; H, 5.50.

$[MoH(CO)_2(diars)_2][SO_3F]$ (3). **3** was prepared analogously to **1**: ^1H NMR (acetone-d_6) τ 15.52; IR (THF solution) 1879 cm^{-1} (vs).

Anal. Calcd for $C_{22}H_{33}As_4FMoO_5S$: C, 32.06; H, 4.04. Found: C, 31.80; H, 3.88.

$[WH(CO)_2(dmpe)_2][SO_3F]$ (4). **4** was prepared analogously to **1**: $^1H\{^{31}P\}$ NMR (acetone-d_6) τ 16.43; IR (THF solution) ν_{CO} 1852 cm^{-1} (vs).

Anal. Calcd for $C_{14}H_{33}FO_5P_4SW$: C, 26.27; H, 5.20. Found: C, 26.81; H, 5.15.

***trans*-$Mo(CO)_2(dmpe)_2$.** To 750 mg of **2** (1.36 mmol) suspended in 15 mL of THF at −78 °C was added 1.40 mL of a 1.00 M solution of potassium in *tert*-butyl alcohol. After warming of the mixture to 5 °C, **2** had completely dissolved, giving a bright yellow solution. After evaporation of the solvent at 5 °C, the residue was stirred with 30 mL of ether and 10 mL of pentane for 5 min at 25 °C. The solution was filtered and the filtrate concentrated at 0 °C to ca. 5 mL. Cooling to −78 °C gave yellow crystals which were collected by filtration, washed with 2 × 2 mL of pentane at −78 °C, and dried in vacuo at 25 °C. The resulting *trans*-$Mo(CO)_2(dmpe)_2$ was stored at −78 °C under N_2 (397 mg, 65%): $^{31}P\{^1H\}$ NMR (benzene) 41.0 (s) ppm;[10] IR (hexane solution) ν_{CO} 1815 (vs) cm^{-1}; mass spectrum *m/e* 452 P^+, 424 $[P - CO]^+$, and 396 $[P - 2CO]^+$.

Anal. Calcd for $C_{14}H_{32}MoO_2P_4$: C, 37.18; H, 7.13. Found: C, 36.91; H, 7.29.

Similarly, addition of potassium *tert*-butoxide to **1**, **3**, or **4** at 0 °C in THF solution resulted in total disappearance of the ν_{CO} of the hydrides and formation of a single new band for the trans isomers: *trans*-$Mo(CO)_2(diphos)_2$, 1823 cm^{-1}; *trans*-$Mo(CO)_2(diars)_2$, 1818 cm^{-1}; *trans*-$W(CO)_2(dmpe)_2$, 1796 cm^{-1}. In each case, refluxing the solution resulted in disappearance of the band for the trans isomers

Table I. Rates of Trans to Cis Isomerization in THF

Compd	10^3k_{obsd}, min^{-1}	$T_{1/2}$,[a] min	Conditions
trans-Mo(CO)$_2$-(dmpe)$_2$[b]	5.02 ± 0.21	138[e]	46.5 °C
	5.15 ± 0.24	135[f]	46.5 °C
trans-Mo(CO)$_2$-(diphos)$_2$[c]	1.88 ± 0.39	369[e]	25.7 °C
	3.34 ± 0.31	208[e]	44.6 °C
	3.22 ± 0.43	215[e]	44.6 °C, 1 atm CO
trans-W(CO)$_2$-(dmpe)$_2$[d]	11.6 ± 2.3	59.8[e]	25.6 °C

[a] Error limits based on standard deviations in least-squares fitting. [b] Followed at 455 nm. [c] Followed at 460 nm; isobestic point at 505 nm. [d] Followed by IR spectroscopy. [e] In the presence of a 10-fold excess of potassium *tert*-butoxide. [f] In the presence of a 20-fold excess of potassium *tert*-butoxide.

and growth of the ν_{CO} of the cis isomers. After conversion was complete, evaporation of the solvent and extraction with benzene gave the pure cis isomers, as judged by comparison of IR and mass spectra with authentic samples.

Kinetic Measurements. An appropriate amount of the hydride was placed in a 25-mL volumetric flask and dissolved in THF in an efficient nitrogen-filled glovebox. An excess of potassium *tert*-butoxide in *tert*-butyl alcohol was added, resulting in an immediate color change. The solution was diluted to the mark and transferred to glass cells, which were degassed, sealed in vacuo, and thermostated. The extent of isomerization was monitored by visible spectroscopy.

Because of the lack of absorbance of *trans*-W(CO)$_2$(dmpe)$_2$ in the visible region, the isomerization was followed by infrared measurements. In this instance a volumetric flask, containing a solution prepared as above, was fitted with a septum and aliquots were withdrawn with a syringe.

Results and Discussion

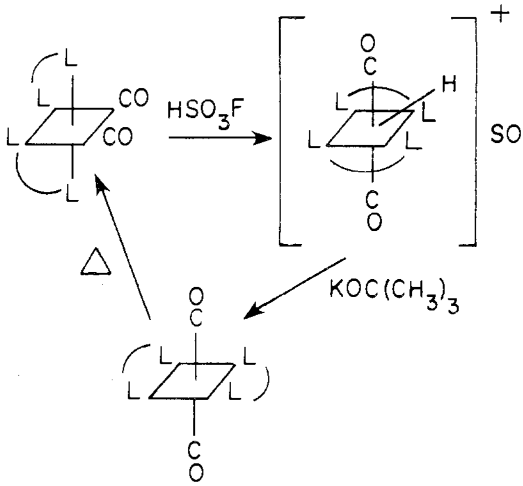
Protonation of *cis*-Mo(CO)$_2$(diphos)$_2$, Mo(CO)$_2$(dmpe)$_2$, Mo(CO)$_2$(diars)$_2$, or W(CO)$_2$(dmpe)$_2$ with HSO_3F under anaerobic conditions affords the corresponding hydrides, **1**–**4**. The dmpe complex [MoH(CO)$_2$(dmpe)$_2$][HCl_2] has been previously reported by Connor et al.[5a] Although deuteration experiments did not locate a metal–hydrogen stretching frequency, each compound exhibited a ^{1}H NMR resonance attributable to the metal hydride. In each case the spectroscopic data imply trans carbonyls and are consistent with the monocapped octahedral structure found for TaH(CO)$_2$(dmpe)$_2$ by x-ray techniques.[6b] In solution, **3** is stable only in the presence of excess acid; the infrared spectrum of a freshly prepared solution in THF slowly reverts to that of *cis*-Mo(CO)$_2$(diars)$_2$.

Deprotonation of **1**, **2**, **3**, or **4** with a stoichiometric amount or excess of potassium *tert*-butoxide quantitatively affords the corresponding *trans*-M(CO)$_2$(L-L)$_2$, identified via IR or ^{31}P NMR spectroscopy. *trans*-Mo(CO)$_2$(dmpe)$_2$ is sufficiently long-lived that it may be easily isolated in crystalline form. *trans*-Mo(CO)$_2$(diphos)$_2$ has been prepared by displacement of N_2 from *trans*-Mo(N$_2$)$_2$(diphos)$_2$[11] and by reduction of [Mo(CO)$_2$(diphos)$_2$][ClO_4].[4b] The former method gives a pure product with, at best, great difficulty.[12] The latter requires preparation of the Mo(I) species.

Inspection of Table I establishes that thermal isomerization of trans **1**, **2**, **3**, and **4** to the cis complexes is sufficiently slow so that the pure isomers prepared by the protonation–deprotonation cycle are amenable to physical or chemical studies. Conversion to the cis isomers follows first-order kinetics and is unaffected by excess base or 1 atm of carbon monoxide. Elson has studied the isomerization of *trans*-Mo(CO)$_2$(diphos)$_2$ (generated in situ by reduction of *trans*-[Mo(CO)$_2$(diphos)$_2$][BF_4]) by electrochemical techniques.[13] Largely on the basis of the increase of k_{obsd} with increasing solvent dielectric constant, an "arm-off, arm-on" mechanism was proposed.[13,14] Our kinetic data are consistent with the trends found by Elson.[15,16]

Aerial oxidation of *cis*-Mo(CO)$_2$(diphos)$_2$ in the presence of perchloric acid is said to give paramagnetic *trans*-[Mo(CO)$_2$(diphos)$_2$][ClO_4],[4a] whereas analogous treatment of *cis*-M(CO)$_2$(dpm)$_2$ (M = Cr, Mo, W; dpm = bis(diphenylphosphino)methane) gives *trans*-[MH(CO)$_2$(dpm)$_2$][ClO_4].[5b] Further, the latter are claimed to be formed via the M(I) complexes, *trans*-[M(CO)$_2$(dpm)$_2$]$^+$, on the basis of ESR evidence.[5b] While this may be true, oxygen is not required for the formation of **1**, **2**, **3**, or **4**—it is, in fact, deleterious. Moreover, Bond et al.[5b] have examined the deprotonation of *trans*-[CrH(CO)$_2$(dpm)$_2$][ClO_4] with tetrabutylammonium hydroxide, which does give *trans*-Cr(CO)$_2$(dpm)$_2$. Oxygen is stated to be necessary for this reaction. Although we have not examined this particular compound, deprotonation of **1**, **2**, **3**, or **4** proceeds rapidly with potassium *tert*-butoxide with rigorous exclusion of air.

Finally, we note that the protonation–deprotonation cycle represents a contrathermodynamic preparation which proceeds because of the geometric preference of the seven-coordinate intermediate.



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Registry No. **1**, 63765-17-3; **2**, 63765-18-4; **3**, 63765-20-8; **4**, 63783-85-7; *trans*-Mo(CO)$_2$(dmpe)$_2$, 63814-04-0; *trans*-Mo(CO)$_2$(diphos)$_2$, 40219-77-0; *trans*-W(CO)$_2$(dmpe)$_2$, 63814-05-1; *trans*-Mo(CO)$_2$(diars)$_2$, 63765-21-9; *cis*-Mo(CO)$_2$(diphos)$_2$, 17523-42-1.

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(16) The small temperature dependence of k_{obsd} for *trans*-Mo(CO)$_2$(diphos)$_2$ is a result of the negative $\Delta S^\ddagger$ for the isomerization.[13]

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Tris(3-nitroso-2,4-pentanedionato)cobalt(III): Strong Evidence for a Facial Geometry Analogous to Ferroverdin

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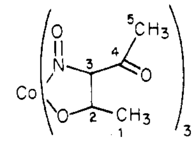
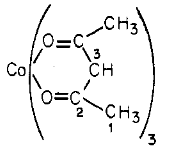
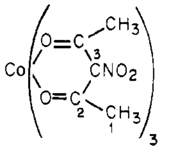
During investigations of the selective interactions of Na[Co^{III}(acac)$_2$(NO$_2$)$_2$]^1 (acac = acetylacetonato) with biomolecules,[2] we neutralized an acid solution of the complex (0.04 mol of complex in 200 mL of 0.8 M HNO$_3$, 15 min) and obtained an orange product, I. This product is soluble in common organic solvents, including CCl$_4$, but insoluble in water or in acid solutions. The material, obtained in 34% yield, was formulated as $C_{15}CoH_{18}N_3O_9$, mol wt 443. Anal. Calcd: C, 40.7; H, 4.1; N, 9.5. Found: C, 40.5; H, 3.9; N, 9.3 [mol wt (cryoscopically, benzene) 407].



I



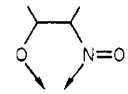
II



III

The IR spectrum of I contains a pronounced carbonyl stretching band at 1715 cm^{-1} (KBr pellet, Perkin-Elmer 621 instrument). The ^{1}H NMR spectrum of I (DCCl$_3$; all ^{1}H and ^{13}C NMR signals in ppm referenced downfield from TMS and obtained using Varian A-60 or CFT-20 instruments) contains only two equal-intensity signals at 2.78 and 2.38 ppm assignable to methyl groups. No signals are present at 5.3 ppm, consistent with the absence of the methine proton at C(3). The addition of strong ligands such as pyridine and tri-*n*-butylphosphine in large excess did not change the ^{1}H NMR spectrum of I.

On the basis of this data, we formulated I as the facial N-bonded isomer of tris(3-nitroso-2,4-pentanedionato)cobalt(III). The properties of this complex correspond exactly with those of that prepared from an authentic sample of 2,3,4-pentanetrione 3-monoxime.[3,4] Furthermore, we were able to recover 2,3,4-pentanedionetrione 3-monoxime[5] from I (in 40% yield) by treatment with sodium sulfide, acidification, extraction into methylene chloride, and addition of ligroin to induce crystallization. Recent studies[4,6] of I and related Co(III) compounds which contain the chelating function agree that coordination to Co(III) involves ligating oxygen and nitrogen atoms.



It is of some interest that studies of Fe(II) and Ni(II) octahedral complexes of chelates which can be expected to coordinate via the N of a nitroso group and by an O forming a five-membered ring also show the formation of the facial isomer.[7-9] One of these compounds,[7] ferroverdin, is a naturally occurring green low-spin iron(II) pigment. The causes for the predominance of the *facial* geometry are not known. However, there have been no previous assignments of the overall geometry of the tris cobalt(III) complexes. On the basis of the ^{1}H NMR data for I, the facial geometry is strongly suggested. In view of the isoelectronic nature of the d^6 Co(III) and Fe(II) centers, we felt it would be worthwhile to further explore the geometry of I and also to investigate one example of the tris(*O*-nitrosophenolate)cobalt(III) complexes which have been so widely studied.[6] The narrow range of chemical shifts and/or ^{1}H,^{1}H couplings of ^{1}H NMR spectra of diamagnetic Co(III) complexes could obscure the presence of a meridional isomer.

The proton-decoupled natural-abundance ^{13}C NMR spectrum of I (DCCl$_3$) contains five distinct signals. The upfield signals at 28.44 and 30.76 ppm are of equal intensity and are readily identified as the C(1) and C(5) methyl carbons of I. For spectral comparison, tris(acetylacetonato)cobalt(III), II, and tris(3-nitroacetylacetonato)cobalt(III),[10] III, were prepared and characterized by elemental analysis. The ^{13}C peak positions are as follows: In II: C(1), 26.06 ppm; C(2), 189.44 ppm; C(3), 97.13 ppm. In III: C(1), 26.42 ppm; C(2), 190.06 ppm; C(3), not observed down to 250 ppm. Both C(1) and C(5) in I are shifted downfield, but an exact assignment of the two upfield signals is not possible. The C(3) signal of II is comparable in intensity to that for C(1), consistent with the presence of a C–H bond at C(3). However, the C(3) signal of I is shifted downfield by almost 60 ppm on nitrosation to 155.58 ppm and is appreciably diminished in intensity as expected from the absence of any C–H bonds. The C(2) resonances in II and III are both at ~189 ppm and the signal of one of the carbonyl carbons of I is also found in this region at 189.01 ppm. We tentatively assign this signal to C(2). The resonance of the other carbonyl carbon, C(4), is found well downfield at 211.34 ppm in a shielding range characteristic of some aliphatic ketones.

The information we have obtained could also be accommodated by a rapidly isomerizing mixture of facial and meridional isomers. However, addition of tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III)[11] (0.03 M) to a solution of I (0.19 M in DCCl$_3$) caused downfield shifts of both methyl ^{1}H NMR resonances (2.38 to 2.96 and 2.78 to 3.28 ppm). The resonance at 3.28 ppm was clearly resolved (~1 Hz) into two signals of equal intensity. Such a finding would require a facile isomerization but a slow racemization—a highly unlikely set of circumstances particularly in view of the known chemistry of cobalt(III) complexes. Similarly, we find that the ^{13}C NMR spectrum of tris(2-nitroso-1-naphtholato)cobalt(III)[6] contains six strong equiintensity signals (corresponding to the six carbons which have a directly bound hydrogen) and two weaker signals (two resonances were not observed). On the basis of the results obtained with I, it is most reasonable to conclude that the complex has the facial geometry.