Substitution Reactions of *mer*-$Cr(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene). Ligand Effects on Diene Binding Preferences

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Received October 17, 1988

Summary: The meridional isomer of $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene) can be made photolytically and has been characterized spectroscopically and crystallographically. The 1,5-COD ligand is readily displaced by conjugated diene ligands as the binding preference of the $Cr(CO)_3(P(OMe)_3)$ fragment is apparently the inverse of $Cr(CO)_4$.

Neutral pseudooctahedral diene complexes of the group 6 metals, with a $ML_4(\eta^4$-diene) stoichiometry, are of interest for their spectroscopy,[1] the exchange reactions of the bidendate diene ligand, and their potential as intermediates in the metal-mediated functionalization of dienes.[2] Work in several laboratories[3] has shown that, for the $M(CO)_4$(diene) case, nonconjugated dienes bind more strongly.[4] It is logical to expect that this preference, as theoretically explained for the d^6 $M(CO)_4$ fragment,[5] is applicable to a variety of L and η-unsaturated ligands. But in fact we discovered that nonconjugated dienes do *not* displace the conjugated diene from $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,3-diene)[6] (1,3-diene = butadiene, isoprene, *trans*-piperylene) and trialkylborohydride reagents attack the terminal carbons of the 1,3-diene complexes to give η^3-allyl complexes instead of the nonconjugated homoallylic complexes.[2] This preference of the $Cr(CO)_3P(OMe)_3$ fragment for conjugated η-unsaturated ligands is indeed thermodynamic, as shown in the present study of the very labile *mer*-$Cr(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene).

Photolysis of a pentane solution of $Cr(CO)_5(P(OMe)_3)$ in the presence of a slight excess of 1,5-cyclooctadiene gives, after recrystallization, $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,5-$C_8H_{12})$ as spectroscopically pure yellow crystals (eq 1).[7] Its small scale preparation and partial spectroscopic characterization have been reported previously by Kreiter.[8]

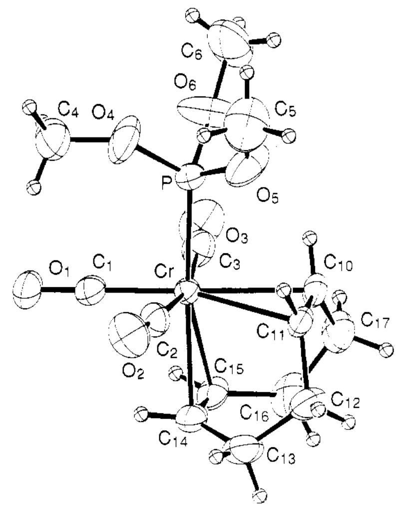

Figure 1. ORTEP drawing of the structure of *mer*-$Cr(CO)_3(P(OMe)_3)(\eta^4$-1,5-cyclooctadiene) with thermal ellipsoids at 30% probability levels. Selected bond lengths (Å) and angles (deg): Cr–P, 2.260 (2); Cr–C_1, 1.813 (8); Cr–C_2, 1.852 (8); Cr–C_3, 1.874 (9); C_1–O_1, 1.172 (8); C_2–O_2, 1.150 (8); C_3–O_3, 1.149 (8); Cr–C_{10}, 2.341 (6); Cr–C_{11}, 2.359 (6); Cr–C_{14}, 2.295 (7); Cr–C_{15}, 2.309 (7); C_{10}–C_{11}, 1.34 (1); C_{14}–C_{15}, 1.35 (1); C_1–Cr–C_2, 84.5 (3); C_1–Cr–C_3 83.7 (3); C_2–Cr–C_3, 165.5 (3); C_1–Cr–P, 85.1 (2); C_3–Cr–P, 87.9 (3).

$$Cr(CO)_5(P(OMe)_3) + 1,5\text{-}C_8H_{12} \xrightarrow[C_5H_{12}]{h\nu} Cr(CO)_3(P(OMe)_3)(\eta^4\text{-}1,5\text{-}C_8H_{12}) + 2\ CO \quad (1)$$

The stereochemistry of the complex in solution is established by IR studies, where three bands at 1980 (m), 1900 (s), and 1890 (ms) cm^{-1} in the ν(CO) stretching region support a localized C_{2v} structure for the three carbonyls. This is also supported by the ^1H COSY spectrum of $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,5-$C_8H_{12})$ (see supplementary material). The *mer* structure persists in the solid state, as shown by a single-crystal X-ray diffraction study.[9] A drawing of the molecule with a listing of important bond lengths and angles is provided in Figure 1. The statistically greater bond lengths to the olefinic carbons trans to the CO reflect its strong trans influence when compared to $P(OMe)_3$ and suggest that that Cr–olefin bond is particularly labile. A similar variation has been found for $Cr(CO)_3(PPh_3)$(norbornadiene).[10]

Trimethyl phosphite reacts stereospecifically with the COD complex to give *mer*-$Cr(CO)_3(P(OMe)_3)_3$,[11] just as

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[1] Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297.

[2] Wink, D. J.; Wang, N.-F.; Springer, J. P. *Organometallics*, in press.

[3] (a) Burkinshaw, P. M.; Dixon, D. T.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1980**, 2237. (b) Tayim, H. A.; Mahmoud, F. T. *J. Organomet. Chem.* **1975**, *92*, 107. (c) Zingales, F.; Canziani, F.; Basolo, F. *J. Organomet. Chem.* **1967**, *7*, 461.

[4] Davis, R.; Kane-Macguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon: New York, 1982; Vol. 3, p 958.

[5] Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, 1058.

[6] This was demonstrated by the absence of change over several days time in the NMR spectrum of a C_6D_6 solution of $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,3-butadiene) in the presence of a large excess of either 1,5-cyclooctadiene or 1,4-pentadiene, conditions under which, for example, the 1,3-butadiene is readily displaced by isoprene.

[7] A solution of 6.73 g (21.3 mmol) of $Cr(CO)_5(P(OMe)_3)$ and 5.2 mL of 1,5-cyclooctadiene (4.6 g, 42 mmol) in 400 mL of pentane was photolyzed for 1 h while the outside of the reactor was cooled by a dry ice/2-propanol bath. The solution turns red during the photolysis. The solution was then concentrated in vacuo to ca. 50 mL at room temperature and then chilled to dry ice temperature. The yellow precipitate was isolated and recrystallized twice from pentane at −25 °C to give spectroscopically pure $Cr(CO)_3(P(OMe)_3)(\eta^4$-1,5-COD) (1.96 g, 25.0%); ^1H NMR (C_6D_6) δ 4.11 (m, 2 H, H_{14}, H_{15}), 3.54 (m, 2 H, H_{10}, H_{11}), 3.33 (d, $^3J_{P-H}$ = 9 Hz, 9 H, $P(OCH_3)_3$), 2.51–2.38 (m, 2 H, H_{12e}, H_{17e}), 2.38–2.25 (m, 2 H, H_{13e}, H_{16e}), 1.69 (m, 2 H, H_{12a}, H_{17a}), 1.50 (m, 2 H, H_{13a}, H_{16a}); ^{13}C NMR (C_6D_6) 235.8 and 235.5 (s, CO), 93.7 and 82.4 (s, *C*–H), 51.8 (d, $P(OCH_3)_3$), 30.1 and 28.6 (s, CH_2); ^{31}P (NMR (C_6D_6) δ 199.6; IR (pentane) ν(CO) 1980 (m), 1900 (s), 1880 (ms) cm^{-1}. Anal. Calcd for $C_{14}H_{21}CrO_6P$: C, 45.65; H, 5.75. Found (Schwatrzkopf): C, 46.19; H, 6.09.

[8] Kreiter, C. G.; Özkar, S. *J. Organomet. Chem.* **1978**, *152*, C13.

[9] The crystal structure of *mer*-tricarbonyl (η^4-1,5-cyclooctadiene)(trimethyl phosphite)chromium(0), $C_{14}H_{21}CrO_6P$, was determined by using a portion of a large needle grown from pentane at −20 °C. Crystals of the compound are formed in the monoclinic space group $P2_1/a$ with a = 13.274 (2) Å, b = 8.920 (1) Å, c = 14.910 (2) Å, β = 107.41 (1)°, and Z = 4. A total of 1881 unique data were collected by using a Rigaku AFC6 diffractometer with Cu Kα radiation using the $\omega-2\theta$ technique in the range $5 < 2\theta < 100.1°$. The structure was solved by using Patterson methods (Calabrese, J. C. Ph.D. Thesis, University of Wisconsin, 1972), the DIRDIF program (Beurskens, P. T. DIRDIF, Direct Methods for Difference Structures; Technical Report 1984/1; Crystallography Laboratory: Toernooiverld, 6525 Ed., Nijimen, Netherlands), and Fourier difference techniques (TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, 1985). Refinement of 199 variables for the positional and anisotropic thermal parameters of all non-hydrogen atoms based on least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ with 1339 reflections with $I > 3\sigma(I)$ converged to a final R value of 5.0% (R_w = 6.6%).

[10] Declerq, P. J. P.; Germain, G.; van Meerssche, M.; Chawdhury, S. A. *Acta Crystallogr.* **1975**, *B31*, 2896.

[11] The reactions proceed to completion with no detectable intermediates, as monitored by ^{31}P NMR, and the tris(phosphite) complexes are identified by comparison with the literature: Bond, A. M.; Carr, S. W.; Colton, R. *Inorg. Chem.* **1984**, *23*, 2343.

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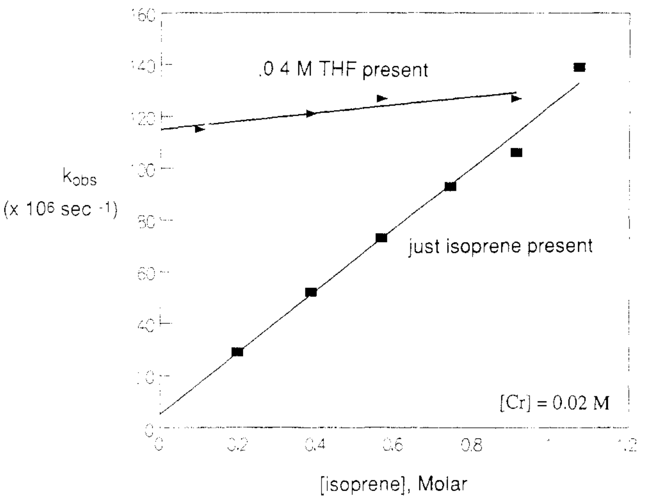


Figure 2. Plot of the pseudo-first-order rate versus isoprene concentration in the presence and absence of added THF. The calculated lines are, in the absence of THF, $k_{\mathrm{obsd}} = \{119\ (7)[\mathrm{isoprene}] + 5\ (4)\} \times 10^{-6}\ \mathrm{s}^{-1}$ and, in the presence of THF, $k_{\mathrm{obsd}} = \{16\ (6)[\mathrm{isoprene}] + 115\ (7)\} \times 10^{-6}\ \mathrm{s}^{-1}$.

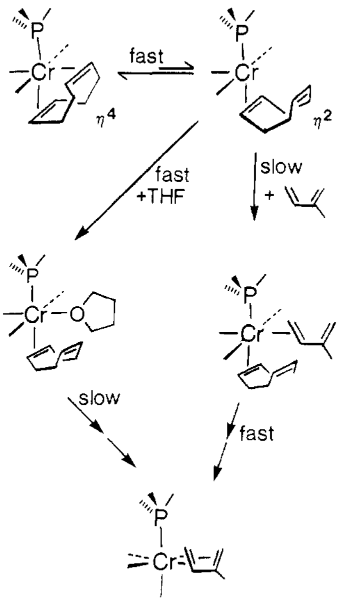
fac-$Cr(CO)_3(P(OMe)_3)(\eta^4$-2-methyl-1,3-butadiene) reacts to give *fac*-$Cr(CO)_3(P(OMe)_3)_3$.[12] The COD ligand is also readily displaced by conjugated dienes such as isoprene, *trans*-piperylene, and even 1,3-cyclohexadiene and trans-1,3,5-hexatriene to give, in solution, the corresponding *fac*-$Cr(CO)_3(P(OMe)_3)$(1,3-diene) complexes (eq 2). Detailed studies of the dependence of the rate of this reaction on ligand concentration are given, for isoprene, in Figure 2.[13]

$$Cr(CO)_3(P(OMe)_3)(\eta^4\text{-}1,5\text{-}C_8H_{12}) + 1,3\text{-diene} \xrightarrow[C_6D_6]{} Cr(CO)_3(P(OMe)_3)(\eta^4\text{-}1,3\text{-diene}) + 1,5\text{-}C_8H_{12} \quad (2)$$

In the absence of THF, the rate is linearly dependent on the concentration of the isoprene, and, within experimental error, the calculated line passes through the origin. A small amount of THF renders the reaction rate essentially independent of the isoprene concentration. The rate profile in the presence of THF is clearly not a superposition of a "THF-assisted" and a "THF-independent" rate and strongly suggests that the mechanistic pathway in the presence of just isoprene is shut down when THF is present.

The mechanistic proposal outlined in Scheme I is consistent with these results and has as a central feature a reactive intermediate (most plausibly an η^2-1,5-COD complex) that can react either in a slow step with isoprene or in a fast step with THF. The present results do not permit an elucidation of the rest of the THF-assisted path, except that the incoming diene may not be involved in the slow step. This scheme is generally consistent with related studies of η^4-ligand substitution with $M(CO)_4$(diene) (M = Cr, Mo, W),[3,14] $Fe(CO)_3$(diene) or $Fe(CO)_3$(enone),[15] and $Co(\eta^5\text{-}C_5H_4X)$(1,5-COD).[16] Note that the formation of a *fac* isomer of the product isoprene complex is in fact uninformative of the mechanism: these molecules are known to be very labile with respect to intramolecular rearrangements.[1]

Scheme I. Mechanistic Scheme for the Diene Exchange Reaction



The inversion of diene binding preference in going from the tetracarbonyl to the tricarbonylphosphite complex is surprising, but it is not in fact in conflict with theory. The study of the tetracarbonyl system by Elian and Hoffmann[5] includes a discussion of the fact that a high-energy pair of electrons is required if a conjugated diene, with its relatively low-lying LUMO, is to bind better than a nonconjugated diene or two isolated olefins, which would be better at σ-donation. Apparently the phosphite adds enough electron density to the metal to stabilize a better π-acceptor ligand. The presence of the meridional isomer is also explicable theoretically. An extended Hückel calculation on the model complex $Cr(CO)_3(P(OH)_3)(C_2H_4)_2$ shows that the *mer* isomer is favored by some 22 kcal/mol over the *fac* isomer, in large part because of increased bonding between the chromium and the phosphorus.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society, and the AMAX Foundation for financial support of this research and to the National Science Foundation for funds to purchase an X-ray diffractometer.

Supplementary Material Available: Details of the assignment of the ^1H NMR spectrum, further details of crystallographic procedures, tables of the atomic positional and thermal parameters and complete bond distances and angles, and drawings of atomic packing (10 pages); a listing of structure factor amplitudes (5 pages). Ordering information given on any current masthead page.

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[12] The meridional isomer of $Cr(CO)_3(P(OMe)_3)_3$ has been shown to be more stable than the *fac*, with the equilibrium constant for the *fac* $\rightleftharpoons$ *mer* reaction of 4.0 (5): Bond, A. M.; Colton, R.; Kevekordes, J. E. *Inorg. Chem.* **1986**, *25*, 749.

[13] Kinetic experiments were run by injecting the appropriate amount of material into a measured amount of the cyclooctadiene complex in C_6D_6 under pseudo-first-order conditions. The reaction was monitored periodically by ^1H NMR, and the changes in the concentration of the starting material was determined by spectral subtraction. All runs were conducted for at least 2 half-lives.

[14] Dixon, D. T.; Kola, J. C.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1307.

[15] Burkinshaw, P. M.; Dixon, D. T.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1980**, 999.

[16] Wakatsuki, Y.; Yamazaki, H.; Kobayashi, T.; Sugawara, Y. *Organometallics* **1987**, *6*, 1191.