

Contribution from the Departments of Chemistry, Cornell University, Ithaca, New York 14853,
and University of Nebraska, Lincoln, Nebraska 68588

Metal Clusters in Catalysis. 20.¹ The Chemistry of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$

LAI-YOONG GOH,² M. J. D'ANIELLO, JR., S. SLATER, E. L. MUETTERTIES,* I. TAVANAIEPOUR,
M. I. CHANG, M. F. FREDRICH, and V. W. DAY*

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Reaction of $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ with 2 mol of trimethyl phosphite at 25 °C yielded the symmetric dimer $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$, **2**. Crystallographic analysis of the dimer established a very long chromium–chromium bond distance of 3.343 Å. Consistent with this distance, the dimer was largely dissociated into the mononuclear fragments, $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3$, in solution at 20 °C and exhibited a high degree of chemical reactivity. Hydrogen addition to **2** was fast at 20 °C to give $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$. Trimethyl phosphite also reacted rapidly with **2**, and cleavage of a C–O bond in a phosphite occurred. The initial products were the methyl complex $\text{C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ and a phosphonate complex $\text{C}_5\text{H}_5\text{Cr}[\text{PO}(\text{OCH}_3)_2](\text{CO})_2\text{P}(\text{OCH}_3)_3$, **3**. An X-ray study of **3** established a square-pyramidal geometry and a trans relationship of the two phosphorus ligands. The methyl complex was unstable and slowly yielded methane at 20 °C. The ionic complex $\{\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}^+ \{\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3\}^-$ formed from **2** by dissolution in polar solvents was a relatively stable and nonreactive complex unlike the molybdenum analogue.

Introduction

Metal clusters present intriguing possibilities in catalysis. If the cluster catalyst precursor remains intact throughout a catalytic cycle, the structural and mechanistic features may, to a first approximation, emulate those of analogous cycles that occur on metal surfaces.^{3–5} If the cluster readily fragments, then there is the potential of generating coordinately unsaturated and highly reactive metal–ligand fragments.^{4,7–9} This article directly addresses the latter possibility. Adams, Collins, and Cotton¹⁰ have shown that the metal–metal bond in $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$, **1**, was the longest (3.281 Å) previously reported transition-metal M–M bond in any dinuclear transition-metal species. Furthermore, they postulated a dissociation of the dimer in solution; the inference was based on the character of the ¹H DNMR spectra. We have tried to exploit the potential of reactive 17- or even 15-electron fragments by increasing the steric crowding in the chromium dimer by trimethyl phosphite substitution of carbonyl groups. A study of $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ has been reported by Haines and Nolte¹¹ with some results formally similar to those from our study. Our present and earlier investigations^{9b} clearly show the potential complexity of a phosphite reaction with transition-metal complexes wherein the phosphite reactant may be incorporated as a P(OR)₃, P(OR)₂, or PO(OR)₂ ligand.

Results and Discussion

$[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$. Reaction of a tetrahydrofuran solution of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$, **1**, with trimethyl phosphite gave the symmetrical trimethyl phosphite derivative $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$, **2**, in a yield of about 50%. This deep green dimer was largely dissociated in solution as judged by a cryoscopic molecular weight determination in benzene and by a susceptibility measurement (Evans' method¹²) at 25 °C. At low temperatures, ~–80 °C, the dimer was not significantly dissociated in toluene-*d*₈ as judged by the relatively sharp C₅H₅ and P(OCH₃)₃ doublet proton NMR resonances. Solid-state susceptibility measurements by Professor D. N. Hendrickson showed that **2** is diamagnetic in the crystalline state.

An X-ray crystallographic study of this phosphite derivative, **2**, showed a close similarity in stereochemical detail (Figure 1) to the parent hexacarbonyl dimer, **1**, but with a substantially longer Cr–Cr' distance of 3.343 (1) Å. Each Cr atom of the centrosymmetric dimer **2** achieves a filled valence-shell electronic configuration by bonding to the other Cr atom through a two-electron single bond, to two terminal carbonyls in a linear fashion, to a trimethyl phosphite phosphorus atom,

and to a cyclopentadienyl ligand in a η^5 fashion. Bond lengths and angles for chemically equivalent groupings: Cr–C (cyclopentadienyl), 2.204 (4, 12, 18, 5) Å;¹³ Cr–C (carbonyl), 1.839 (4, 2, 2, 2) Å;¹³ Cr–P, 2.238 (1) Å; P–O, 1.596 (3, 4, 6, 3) Å; C–O (carbonyl), 1.160 (5, 4, 4, 2) Å; O–C (phosphite), 1.44 (7, 17, 26, 3) Å; C–C, 1.398 (7, 6, 12, 5) Å; CpCrC (carbonyl),¹⁴ 126.1 (... , 1, 1, 2);¹³ CpCrP, 115.0°; CpCrCr', 115.5°; PCrCr', 129.5 (1)°; PCrC (carbonyl), 81.0 (1, 8, 8, 2);¹³ CCrC (carbonyl), 106.6 (2)°; Cr'CrC (carbonyl), 69.8 (1, 8, 8, 2)°; CrCO (carbonyl), 174.6 (4, 5, 5, 2)°; CrPO, 118.5 (1, 43, 65, 3)°; OPO, 99.3 (2, 63, 94, 3)°; POC, 123.6 (4, 17, 25, 3)°.¹⁵ Cotton noted¹⁰ that the unfavorable intramolecular contacts between cyclopentadienyl and CO ligands on adjacent metals were probably responsible for the considerable elongation of the Cr–Cr bond beyond a normal single-bond value in the parent dimer **1**. The 0.06 Å elongation of the Cr–Cr' bond in **2** relative to **1** is presumably the result of additional steric crowding associated with replacement of a compact CO ligand with a considerably bulkier trimethyl phosphite ligand. Steric considerations would preclude the replacement of more than one carbonyl group on each metal by a bulky phosphine or phosphite ligand if a dimeric species which contains a two-electron single bond between the two Cr atoms is to be maintained. In fact, the phosphite-substituted dimer **2** reacts irreversibly with additional trimethyl phosphite at 25 °C to give radical-substituted mononuclear chromium complexes.

Dimer **2** was obtained in good yield only when a stoichiometric amount of trimethyl phosphite reagent was employed. In contrast, Haines and Nolte¹¹ found that the analogous thermal reaction¹¹ of $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ with trimethyl phosphite at 25 °C yielded $\{\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}^+ \{\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\}^-$. Synthesis of the molybdenum dimer analogous to **2**, $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$, required ultraviolet irradiation for 5–15 h of a 1:2 reaction mixture of $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ with trimethyl phosphite.¹¹ Properties were not reported for this specific dimer, but the corresponding triethyl, triisopropyl, and tri-*n*-butyl phosphite derivatives were all reported to be dimeric in benzene solution and were diamagnetic in these solutions at 25 °C as judged by the NMR spectra.¹¹

The other products produced in the stoichiometric reaction of **1** with trimethyl phosphite at 20 °C were the 1:1 electrolyte $\{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}^+ \{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\}^-$, $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$, $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$, $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})[\text{P}(\text{OCH}_3)_3]_2$, and a phosphonate derivative, $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3\text{P}(\text{O})(\text{OCH}_3)_2$, **3**, discussed below.

$[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}^+ \{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\}^-$. In polar solvents, the symmetric dimer **2** underwent internal electron

* To whom correspondence should be addressed: E.L.M., Department of Chemistry, University of California, Berkeley, CA 94720; V.W.D., University of Nebraska.

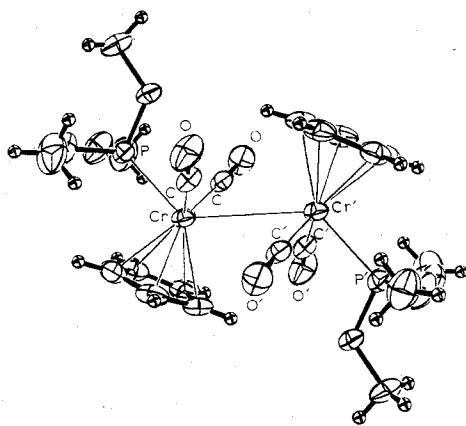


Figure 1. Perspective ORTEP drawing of the $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$ molecule, **2**. All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion. Atoms labeled with primes are related to those without primes by the crystallographic inversion center midway between the two Cr atoms.

transfer with concomitant ligand-exchange reactions to form the 1:1 electrolyte $\{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}^+\{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\}^-$. This ionic complex displayed little reactivity toward excess trimethyl phosphite at 25 °C; in acetonitrile, over half of the ionic complex survived exposure to excess trimethyl phosphite over a 3-day period.

Reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$ with Trimethyl Phosphite. Trimethyl phosphite reacted rapidly with $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$ with cleavage of a phosphite O-CH₃ bond to primarily form a neutral methylchromium(II) complex, $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ in cis and trans stereoisomeric form, and a trans phosphonate species of elementary composition, $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{OP}(\text{OCH}_3)_2]\text{P}(\text{OCH}_3)_3$, **3**. Small amounts of a carbonyl insertion product, $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{COCH}_3)(\text{CO})\text{P}(\text{OCH}_3)_3$, and a hydride derived from the decomposition of the methyl complex, $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$, were also present in the reaction mixtures.

For the methyl, acetyl, and hydride derivatives, the basic structure should be **4** or **5** with cis or trans arrangement,

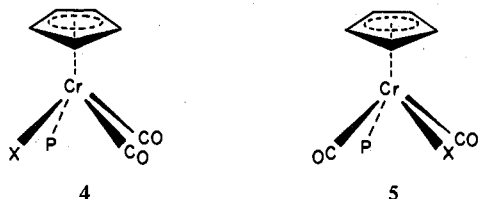
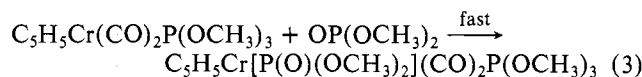
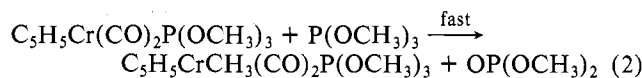
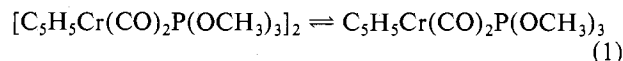


Figure 2. Perspective ORTEP drawing of the nonhydrogen atoms for one of the two crystallographically independent molecules found in single crystals of $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{PO}(\text{OCH}_3)_2]\text{P}(\text{OCH}_3)_3$, **3**. The stereochemistry of the second molecule differs from this one only in the orientations of the trimethyl phosphite methyl groups. All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density.

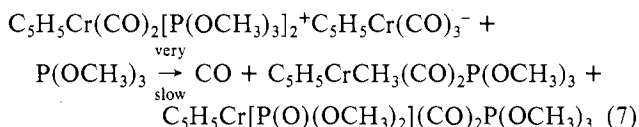
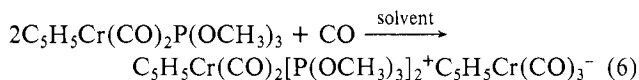
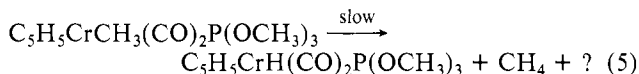
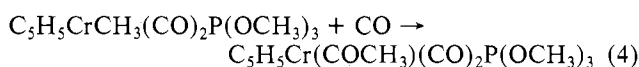
and to a cyclopentadienyl ligand in a η^5 fashion. The crystal of **3** used for this study contained two crystallographically independent molecules in the asymmetric unit which were nearly isostructural; even the orientations of the cyclopentadienyl, trimethyl phosphite, and phosphonate ligands were similar. The only significant structural differences between the two molecules involved the orientations of the trimethyl phosphite methyl groups. Average bond lengths and angles for chemically distinct groupings in the two molecules:¹⁵ Cr-C (cyclopentadienyl), 2.202 (10, 11, 22, 10) Å;¹³ Cr-C (carbonyl), 1.883 (10, 10, 20, 4) Å; Cr-P₁ (phosphonate), 2.360 (3, 1, 1, 2) Å; Cr-P₂ (phosphite), 2.267 (3, 2, 2, 2) Å; P₁=O (phosphonate), 1.478 (6, 6, 6, 2) Å; P₁-O (phosphonate), 1.613 (6, 4, 5, 4) Å; P₂-O (phosphite), 1.581 (7, 10, 21, 6) Å; C-O (carbonyl), 1.141 (10, 10, 19, 4) Å; C-O (phosphite and phosphonate), 1.434 (10, 25, 82, 10) Å; C-C (cyclopentadienyl), 1.421 (15, 19, 48, 10) Å; CpCrC (carbonyl),¹⁴ 122.5 (... , 1, 1, 2)°; CpCrP₁,¹⁴ 112.1 (... , 2, 2, 2)°; CpCrP₂,¹⁴ 115.4 (... , 3, 3, 2)°; P₁CrP₂, 132.5 (1, 6, 6, 2)°;¹³ CCrC (carbonyl), 114.7 (4, 1, 1, 2)°; P₁CrC (carbonyl), 75.9 (2, 12, 16, 4)°; P₂CrC (carbonyl), 79.1 (2, 4, 6, 4)°; CrCO (carbonyl), 176.8 (8, 10, 19, 4)°; CrP₁O₁ (phosphonate), 118.8 (3, 1, 1, 2)°; CrP₁O, 107.8 (2, 16, 18, 4)°; CrP₂O, 116.5 (2, 36, 47, 6)°; O₁P₁O (phosphonate), 110.1 (3, 4, 7, 4)°; OPO (phosphonate and phosphite), 101.4 (4, 24, 40, 8)°.

NMR studies of the trimethyl phosphite reactions with $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$ in benzene showed the methyl and the phosphonate chromium derivatives to be the primary reaction products. In polar solvents like acetonitrile, the symmetric dimer was partially converted to the complex salt $\{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}^+\{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\}^-$; then subsequent addition of trimethyl phosphite immediately converted the remaining symmetric dimer to the methyl and phosphonate derivatives. On standing in solution, the methyl derivative was slowly converted to the hydride $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$, and the complex salt was very slowly converted to the phosphonate and methyl derivatives. These reactions are summarized in eq 1-7. The formation of the



respectively, of the phosphite ligand. Such pseudo-square-pyramidal geometry is well established for $\eta^5\text{-C}_5\text{H}_5\text{ML}_4$ complexes.¹⁶

The NMR spectrum of the phosphonate derivative showed spin-spin coupling of the C₅H₅ protons with both the phosphorus atoms in the OP(OCH₃)₂ and the P(OCH₃)₃ ligands. Since H-P coupling through a C₅H₅CrOP sequence was expected to be very small, a Cr-P(O)(OCH₃)₂ bonding of this phosphorus ligand seemed most likely. This was confirmed for the solid state by a crystallographic study of this compound. Single crystals of **3** were composed of discrete monomeric $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{PO}(\text{OCH}_3)_2]\text{P}(\text{OCH}_3)_3$ molecules (Figure 2) which exhibited the trans arrangement shown in **5** for the two carbonyl ligands. The Cr atom achieves a filled valence-shell electronic configuration by bonding to the phosphorus atoms of a trimethyl phosphite ligand and a phosphonate radical, to two terminally bonded carbonyl ligands,



methyl and phosphonate derivatives could be based on reaction of the monomeric, as depicted in (2) and (3), or the dimeric $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3$ molecules; the former is the predominant solution species.

Reaction of the symmetric dimer with $\text{P}(\text{OCD}_3)_3$ at 1:2 molar ratios in acetonitrile gave the phosphonate derivative with $\text{OP}(\text{OCH}_3)_2\text{OP}(\text{OCD}_3)_2$ ratios of $\sim 1:1.2$ and the methyl derivative with $\text{CH}_3:\text{CD}_3$ ratios of ~ 1.1 . In a modification of this reaction, the symmetric dimer was dissolved in acetonitrile and allowed to stand for 8 h or more—so as to generate substantial quantities of $\{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{-}[\text{P}(\text{OCH}_3)_3]_2\}^+ \{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\}^-$ —before $\text{P}(\text{OCD}_3)_3$ was added. Under these conditions and 1:2 molar ratios, the products after 20 h or more had nearly 1:1 (1:1 to 1:1.3) ratios of CH_3 to CD_3 in the methyl derivative and of $\text{OP}(\text{OCH}_3)_2$ to $\text{OP}(\text{OCD}_3)_2$ in the phosphonate derivative. The $\text{CH}_3:\text{CD}_3$ ratios were directly dependent upon the $\text{P}(\text{OCD}_3)_3$ concentration. The formation of CrCH_3 and $\text{Cr}[\text{P}(\text{O})(\text{OCH}_3)_2]$ species in the $\text{P}(\text{OCD}_3)_3$ reaction suggests a preexchange of phosphite ligand competitive with the O-CH_3 cleavage reaction possibly in a $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3\text{P}(\text{OCD}_3)_3$ intermediate.

A species like $\{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}^+$ would seem quite appropriate for a methyl cation transfer. However, this salt itself was stable in solution and only slowly reacted with an excess of trimethyl phosphite. Since the methyl and the phosphonate complexes that are rapidly formed from the symmetric dimer and $\text{P}(\text{OCD}_3)_3$ are largely derived from the perdeuteriotrimethyl phosphite, the dominant reaction sequence probably involves phosphite attack of the monomeric $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3$ species. Haines and Nolte¹¹ proposed that in the molybdenum system the ionic complex $\{\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{OR})_3]_2\}^+ \{\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\}^-$ reacted with trimethyl phosphite at $\sim 70^\circ\text{C}$ to give the methyl complex $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OR})_3$ and an analogous phosphonate complex, $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{P}(\text{O})(\text{OCH}_3)_2)(\text{CO})\text{P}(\text{OCH}_3)_3$. The same products were obtained from $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ and excess phosphite at $\sim 70^\circ\text{C}$. In the absence of free phosphite, the ionic molybdenum complex decomposed in solution at $\sim 70^\circ\text{C}$ to give the phosphonate compound and $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CH}_3)(\text{CO})_3$. Thus, despite the overall formal analogy between the chromium and molybdenum systems, the kinetic and reaction mechanistic features are substantially different.

Chemistry of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$. The dimer reacted quantitatively with hydrogen at 20°C to form $\text{C}_5\text{H}_5\text{CrH}(\text{CO})_2\text{P}(\text{OCH}_3)_3$. A similar behavior was observed for the parent dimer $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$, but formation of $\text{C}_5\text{H}_5\text{CrH}(\text{CO})_3$ was incomplete even after 16 h at 20°C . Neither of these dimers were active catalyst precursors for the hydrogenation of either 3-hexyne or 1-hexene at $20\text{--}60^\circ\text{C}$. The corresponding hydrides were recovered from these reactions along with unchanged 3-hexyne and 1-hexene, respectively.

Chemistry of $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$. The methyl complex reacted with carbon monoxide with insertion to yield

the acetyl derivative $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{COCH}_3)(\text{CO})_2\text{P}(\text{OR})_3$. This complex was a mixture of trans and cis isomers with the former predominant by a factor of almost 3. Under the conditions of the trimethyl phosphite- $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$ reaction, some carbon monoxide was liberated and then scavenged by the methyl derivative to form small, but detectable, amounts of the acetyl derivative.

In solution, there was a slow decomposition of the methyl complex to give methane and the hydride $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$. Decomposition in a perdeuteriobenzene solvent yielded no deuterium incorporation in the methane produced. At 75°C , the decomposition of the methyl complex was complete within 24 h; in addition to methane and the hydridochromium complex, the acetylchromium complex and the cyclopentadiene dimer were identified as major products. Another product must be formed in the decomposition of the methylchromium complex, but all attempts to isolate and characterize this species were unsuccessful.

In reactions of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ effected in the presence of excess trimethyl phosphite, another hydride, $\eta^5\text{-C}_5\text{H}_5\text{CrH}(\text{CO})[\text{P}(\text{OCH}_3)_3]_2$, was formed. Koola and Brintzinger¹⁷ earlier reported the synthesis of this hydride by reaction of $\eta^5\text{-C}_5\text{H}_5\text{CrH}[\text{P}(\text{OCH}_3)_3]_3$ with carbon monoxide.

Experimental Section

All procedures were carried out either in an argon or a nitrogen atmosphere in a Vacuum Atmospheres drybox with a Model HE 493 Dri-Train or in a conventional vacuum system.

Reagents and Solvents. Trimethyl phosphite was degassed, dried over sodium, and then distilled prior to use. Solvents were refluxed over calcium hydride and were distilled prior to use. Silica gel was activated at 120°C for 1 day before chromatographic use.

Physical Measurements. Proton NMR spectra were recorded at ambient temperature, unless otherwise noted, on a Varian EM390 or Bruker HFX 90 spectrometer. Chemical shifts are referenced to $(\text{CH}_3)_4\text{Si}$ and the solvent was C_6D_6 , CD_3CN , or C_7D_8 . Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrometer.

Methanes were characterized on a Perkin-Elmer 990 gas chromatograph, a Finnegan 3300 GC-MS interfaced with a System Industries system, and an MS-9 mass spectrometer. Elemental analyses and molecular weight determinations were made by Franz Pascher Laboratories, Bonn, Germany.

Synthesis and Characterization of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$. The procedure of King and Stone¹⁸ was modified and employed 0.04-mol quantities of sodium cyclopentadienylchromium tricarbonyl and allyl chloride. The reaction was allowed to proceed at 25°C for 24 h. The crude product was twice sublimed at $90\text{--}100^\circ\text{C}$ (0.05 mm) to give deep green crystals of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ (3.5 g, 43% yield; the yields dropped to $\sim 25\%$ with reaction times of ~ 2 h when allyl bromide was used. IR (Nujol): $\nu(\text{CO})$ 1935 (s), 1920 (s), 1880 (s) cm^{-1} . IR (benzene solution): $\nu(\text{CO})$ 2010 (m), 1945 (s), 1925 (s), 1910 (sh) cm^{-1} . The mass spectrum was very sensitive to the ionization voltage and the inlet temperature. Principal mass ions at 20 eV and a 130°C probe temperature were assigned to $(\text{C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_3^+$ (57%), $(\text{C}_5\text{H}_5)_2\text{Cr}^+$ (51%), $\text{C}_5\text{H}_5\text{CrC}_5\text{H}_4^+$ (100%), $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2^+$ (25%), $\text{C}_5\text{H}_5\text{Cr}^+$ (65%), and Cr^+ (49%). The effective magnetic moment of the monomer assumed to be present in solutions of the dimer was too low for measurement by the Evans NMR method.

Reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ with 2 Equiv of $\text{P}(\text{OCH}_3)_3$. Trimethyl phosphite (0.62 mL, 5.0 mmol) was injected into a Schlenk flask that contained a solution of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2$ (2.5 mmol) in 250 mL of tetrahydrofuran. The solution was magnetically stirred during the injection and the subsequent reaction period. The color of the solution changed from a dark green to a "muddy" green as CO evolved. Gas evolution slowed after ~ 20 min. The solvent was then quickly removed under vacuum at 25°C . A mixture of green and yellow microcrystals remained. The green crystals were recovered by benzene dissolution. The crude product was chromatographed on a silica gel column (8 in. by 0.8 in.) that had been deactivated with ether and then washed with hexane. This complex eluted with hexane, hexane-benzene, and benzene. Recrystallization of the complex from a tetrahydrofuran-hexane mixture at 0°C gave deep green crystalline platelets (0.65 g, 1.1 mmol; 44% yield). Anal. Calcd for $[\eta^5\text{-}$

$C_5H_5Cr(CO)_2P(OCH_3)_3)_2$: C, 40.42; H, 4.75; P, 10.42; Cr, 17.50. Found: C, 40.51; H, 4.69; P, 10.15; Cr, 16.78. 1H NMR (C_6D_6 , Me_4Si): δ -3.9 (vbr). 1H NMR (C_7D_8 , Me_4Si , $-89^\circ C$): δ -5.14 (d, 5 H), -3.49 (d, $J_{PH} = 11.5$ Hz, 9 H). The magnetic moment, determined by the Evans NMR method, was 1.3 and $1.4 \mu_B$ in C_6D_6 and CD_3CN , respectively. The molecular weight (cryoscopic in C_6H_6 , 3.918 mg in 0.3 mL) was 287 as compared to a 297 theoretical value for a monomer. IR (hexane): $\nu(CO)$ 1945 (vs), 1910 (w, sh), 1940 (vs) cm^{-1} . Susceptibility measurement (by Professor D. N. Hendrickson): μ_{eff} varied from 0.44 to $0.27 \mu_B$ between 285 and 4.2 K. The average value of $0.3 \mu_B$ is just the temperature-independent paramagnetism.

In addition to the dimer **2**, the following products (characterized in later sections) were isolated by column chromatography with a silica gel support: $\eta^5-C_5H_5Cr(CH_3)(CO)_2P(OCH_3)_3$ (5%), $\eta^5-C_5H_5Cr(COCH_3)(CO)_2P(OCH_3)_3$ (3.0%), $\eta^5-C_5H_5Cr[PO(OCH_3)_2](CO)_2P(OCH_3)_3$ (13%), $\{\eta^5-C_5H_5Cr(CO)_2[P(OCH_3)_3]_2\}^+[\eta^5-C_5H_5Cr(CO)_3]^-$ (4%), and traces of the hydrides $\eta^5-C_5H_5Cr(H)(CO)_x[P(OCH_3)_3]_{3-x}$ ($x = 1, 2$). The yield of the dimer was sensitive to reaction temperature and to reaction stoichiometry. With reaction temperatures $>25^\circ C$, the yield of **2** dropped substantially. Condensation of the phosphite over $[\eta^5-C_5H_5Cr(CO)_3]_2$ followed by slow warming gave the salt $\{\eta^5-C_5H_5Cr(CO)_2[P(OCH_3)_3]_2\}^+[\eta^5-C_5H_5Cr(CO)_3]^-$ in 60% yield.

Reaction of $[\eta^5-C_5H_5Cr(CO)_3]_2$ with Excess Trimethyl Phosphite. Trimethyl phosphite (2.0 mL, 16 mmol) was injected into a 300-mL Schlenk flask that contained a solution of $[\eta^5-C_5H_5Cr(CO)_3]_2$, 2 mmol in 200 mL of tetrahydrofuran. The solution was magnetically stirred. Solution color changed rapidly from a deep green to an orange-yellow as carbon monoxide evolved over a 10–15 min period. Solvent was then rapidly removed under vacuum to leave a residual volume of ~ 2 mL. To the residual solution were added 20 mL of ether and 5 mL of pentane. The solution was stored at $0^\circ C$ for ~ 16 h. Filtration gave yellowish brown crystals and a "mother liquor".

The brown-yellow crystalline mixture was separated as follows. A benzene-tetrahydrofuran extraction left yellow crystals that were recrystallized from an acetonitrile-tetrahydrofuran-hexane mixture at $0^\circ C$ to give golden platelets of $\{\eta^5-C_5H_5Cr(CO)_2[P(OCH_3)_3]_2\}^+[\eta^5-C_5H_5Cr(CO)_3]^-$ (50 mg, 5% yield). Anal. Calcd for $C_{21}H_{28}Cr_2O_{11}P_2$: C, 40.53; H, 4.53; Cr, 16.71; P, 9.95. Found: C, 40.59; H, 4.48; Cr, 16.14; P, 10.35. 1H NMR (CD_3CN , Me_4Si): δ -4.94 (t, $J_{PH} = 1.8$ Hz, 5 H), -4.28 (s, 5 H), -3.67 (m, $J_{PH} = 11.1$ Hz, 18 H). IR (tetrahydrofuran): $\nu(CO)$ 1990 (w, sh), 1980 (m), 1960 (w, sh), 1915 (s), 1880 (vs), 1775 (vs) cm^{-1} . Conductivity in CH_2Cl_2 : $1.657 \times 10^{-3} M$, $\Lambda_{molar} = 18.43 \Omega^{-1} mol^{-1}$. The range for 1:1 electrolytes is ~ 10 – $50 \Omega^{-1} mol^{-1}$.

The brownish benzene-tetrahydrofuran solution from the above separation was concentrated to near dryness; the residue was dissolved in a minimum of benzene. This solution was introduced on a silica gel chromatographic column that had been deactivated with ether and then washed with benzene. Elution with benzene (~ 30 mL) and then with a 1:9 ether-benzene mixture yielded a green oil that consisted largely of $[\eta^5-C_5H_5Cr(CO)_2P(OCH_3)_3]_2$ (~ 0.04 mmol) with some of the acetyl and hydride complexes described below. Elution with tetrahydrofuran (30 mL) followed by acetonitrile yielded an orange-yellow oil that contained $[\eta^5-C_5H_5Cr(CO)_2[P(OCH_3)_3]_2]^{+}[\eta^5-C_5H_5Cr(CO)_3]^{-}$ and two other unidentified complexes. The column was removed from the inert-atmosphere box, and the remaining blue-green band was eluted with 80 mL of methanol to give a yellow solution. Concentration of the yellow solution yielded an air-stable solid. This solid was sublimed at $95^\circ C$ (0.1 mm) (0.6 g, 37% yield). The solid was recrystallized from a tetrahydrofuran-hexane solution which gave yellow single crystals. Anal. Calcd for $C_5H_5Cr(CO)_2[PO(OCH_3)_2]P(OCH_3)_3$: C, 35.48; H, 4.96; P, 15.25; Cr, 12.80; $M_r = 406.24$. Found: C, 35.68; H, 4.94; P, 15.63; Cr, 12.46; M_r (cryoscopic in C_6H_6 , 4.1999 mg in 0.6 mL) = 450. 1H NMR (C_6D_6 , Me_4Si): δ -4.67 (dd, $J_{PH} = 1.0$ Hz, $J_{PH} = 2.0$ Hz, 5 H), -3.93 (d, $J_{PH} = 11.0$ Hz, 6 H), -3.37 (d, $J_{PH} = 11.4$ Hz, 9 H). 1H NMR (CD_3CN , Me_4Si): δ -4.67 (d, $J_{PH} = 1.8$ Hz, 5 H), -3.46 (d, $J_{PH} = 11.0$ Hz, 6 H), -3.50 (d, $J_{PH} = 11.0$ Hz, 9 H). IR (tetrahydrofuran): $\nu(CO)$ 1955 (m), 1890 (vs), 1870 (vw, sh) cm^{-1} .

The mother liquor from the above original separation of solids was concentrated under vacuum and then dissolved in ~ 2 mL of hexane. This hexane solution was placed on a silica gel chromatographic column that had been deactivated with ether. Elution yielded the following fractions:

Table I

complex	peak ratios		
	22 h	43 h	78 h
1:1 ionic compl	23	22	19
phosphonate compl	32	34	34
methyl compl	3	3	3
cis	12	10	10
trans	12	10	10
hydride + acetyl compl	22	23	25

Table II

complex	peak ratios		
	1.25 h	7 h	78 h
1:1 ionic compl	34	18	14
phosphonate compl	21	27	26
methyl compl	4	5	5
cis	16	24	17
trans	16	24	17
hydride + acetyl compl	14	14	17

Hexane-benzene (1:1 v/v, 50 mL) elution followed by benzene (30 mL) yielded a yellow solution of $\eta^5-C_5H_5Cr(CH_3)(CO)_2P(OCH_3)_3$ contaminated with a trace of $\eta^5-C_5H_5Cr(H)(CO)_2P(OCH_3)_3$. Sublimation at $30^\circ C$ (0.1 mm) gave as a thermally unstable yellow solid $\eta^5-C_5H_5Cr(CH_3)(CO)_2P(OCH_3)_3$ (0.8 mmol, 20% yield). Mass spectrum (70 eV, $80^\circ C$ probe): $C_5H_5Cr(CH_3)(CO)_2P(OCH_3)_3^+$, $C_5H_5Cr(CO)_2P(OCH_3)_3^+$, $C_5H_5Cr(CH_3)(CO)P(OCH_3)_3^+$, $C_5H_5Cr(CO)P(OCH_3)_3^+$, $C_5H_5Cr(CH_3)P(OCH_3)_3^+$, $C_5H_5Cr(H)P(OCH_3)_3^+$, $C_5H_5CrCH_3^+$. 1H NMR (C_6D_6 , Me_4Si): trans: δ -4.28 (d, $J_{PH} = 2.7$ Hz, 5 H), -3.36 (d, $J_{PH} = 11.4$ Hz, 9 H), -0.93 to -0.75 (d, $J_{PH} = 1.8$ Hz, 3 H); cis: δ -4.36 (d, $J_{PH} = 1.2$ Hz, 5 H), -3.36 (d, $J_{PH} = 11.4$ Hz, 9 H), -0.055 to -0.40 (d, $J_{PH} = 9.5$ Hz, 3 H). All doublets were converted to singlets in the $^1H\{^31P\}$ experiment. IR (hexane): $\nu(CO)$ 1950 (s), 1880 (vs), 1860 (w, sh). An additional 0.1 mmol (2.5% yield) of the methyl complex was obtained by column washing with 10% benzene in ether (50 mL).

Elution with tetrahydrofuran-acetonitrile mixtures (60 mL) gave a small amount of an orange-yellow solution of a chromium complex that contained no C_5H_5 ligands and left a small amount of phosphonate complex on the column.

Reaction of $[\eta^5-C_5H_5Cr(CO)_2P(OCH_3)_3]_2$ with $P(OCH_3)_3$ —NMR Study. To a solution of $[C_5H_5Cr(CO)_2P(OCH_3)_3]_2$ (0.37 mmol) in 0.5 mL of C_6D_6 in an NMR tube was added 30 μL (0.255 mmol) of $P(OCH_3)_3$. Reaction was immediate. Product concentrations were determined from the intensities of the C_5H_5 proton resonances (standardized with 5 μL of C_6H_6 that was added after completion of the reaction). Products after 15 h were $C_5H_5Cr(CO)_2[PO(OCH_3)_2]P(OCH_3)_3$ (50%), $C_5H_5Cr(CH_3)(CO)_2P(OCH_3)_3$ (cis 10%, trans 30%), $C_5H_5(COCH_3)(CO)_2P(OCH_3)_3$ (5%), and $C_5H_5Cr(H)(CO)_2P(OCH_3)_3$ (5%).

The above experiment was repeated with 0.044 mmol of the dimer and 0.24 mmol of $P(OCD_3)_3$ (mole ratio of 1:5.46). Reaction was immediate (clear yellow solution). An unidentified C_5H_5 doublet resonance was detected; the relative concentration of this species fell from 7 to 0% in 1.5 h. The concentration of the phosphonate derivative was nearly constant over 15 h ($50 \pm 2\%$), while the concentration of the methyl complex was $\sim 48\%$ for the first 0.5 h and then dropped to 42% (35% trans) after 15 h. The acetyl and hydride resonances were not detected until about 1-h reaction times (4 and 1.5%, respectively). After 1 h, the hydride resonance grew in intensity; final relative concentration was 3%. The ratios $PO(OCH_3)_2:PO(OCD_3)_2$ and $CH_3:CD_3$ in the phosphonate and methyl complexes, respectively, were about 1:4.

A solution of $[C_5H_5Cr(CO)_2P(OCH_3)_3]_2$ (0.0375 mmol) in CD_3CN (0.5 mL) was allowed to stand at $25^\circ C$ for 8 h. At the end of this time, the solution contained $\sim 60\%$ of the initial dimer and 40% of $[C_5H_5Cr(CO)_2[P(OCH_3)_3]_2]^{+}[C_5H_5Cr(CO)_3]^{-}$. At this point, trimethyl phosphite (0.08 mmol) was added and the characteristic proton resonances were monitored after different reaction intervals. Results are given in Table I (relative peak ratios). A similar experiment with immediate mixing of the reactants gave the results in Table II. Each of these experiments was repeated with $P(OCD_3)_3$. The ratios $PO(OCH_3)_2:PO(OCD_3)_2$ and $CH_3:CD_3$ in the phosphonate and methyl complexes were 1:1.2 and 1:1, respectively, when the phosphite was added directly to the reaction mixture. When the addition was delayed for 8 h, the resultant $CH_3:CD_3$ ratio in the methyl complex was 1:1.27,

Table III

complex	peak ratios		
	3 h	7 h	50 h
ionic compl	23	18	14
phosphonate compl	28	28	28
methyl compl	5	6	5
cis	21	23	21
trans	12	14	16
hydride + acetyl compl			

1:1, and 1:1 after 22, 43, and 70 h, respectively.

A solution of $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$ (0.04 mmol) in CD_3CN (0.5 mL) was allowed to stand for 60 h. Solvent was removed under vacuum. C_6D_6 (0.5 mL) was added (a slight oil film did not dissolve), and 0.05 mmol of $\text{P}(\text{OCD}_3)_3$ was added. Concentrations of complexes were followed by NMR over a 50-h reaction period. Results are given in Table III. The ratios $\text{PO}(\text{OCH}_3)_2:\text{PO}(\text{OCD}_3)_2$ and $\text{CH}_3:\text{CD}_3$ in the phosphonate and methyl complexes were $\sim 1:1.27$ at 50 h.

Reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2]_2$ with Excess $\text{P}(\text{OCH}_3)_3$ at 65 °C. Trimethyl phosphite (0.5 mL, 4 mmol) was added to a solution of the dimer (0.20 g, 0.5 mmol) in 60 mL of tetrahydrofuran; the color changed from deep green to a yellow-green. The reaction mixture was heated to reflux for 7 h; the color was brownish red. The solvent was removed under vacuum at 25 °C. Chromatographic separation of the reaction products was effected on alumina deactivated with ether and washed with benzene. Two main fractions were obtained. Elution with 1:1 pentane-benzene gave a yellow-green oil that consisted of a mixture of $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{PO}(\text{OCH}_3)_2]\text{P}(\text{OCH}_3)_3$ (50%), $\text{C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ (5%), and $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$ (40%). Spectral data for the hydride are given as follows. ^1H NMR (C_6D_6 , Me_4Si): δ -4.43 (d, $J_{\text{PH}} = 1.2$ Hz, 5 H), -3.33 (d, $J = 11.1$ Hz, 9 H), +7.1 (d, $J_{\text{PH}} = 87$ Hz). IR (hexane): $\nu(\text{CO})$ 1950 (vs), 1890 (vs) cm^{-1} . Elution with 1:1 benzene-ether gave a yellow-green oil that was largely $\text{C}_5\text{H}_5\text{Cr}(\text{H})\text{CO}[\text{P}(\text{OCH}_3)_3]_2$ (0.04 mmol, 4% yield). ^1H NMR (C_6D_6 , Me_4Si): δ -4.54 (t, $J_{\text{PH}} = 1.5$ Hz, 5 H), -3.48 (d, $J_{\text{PH}} = 11.0$ Hz, 18 H), +8.7 (t, $J_{\text{PH}} = 97$ Hz, 1 H). IR (hexane): $\nu(\text{CO})$ 1950 (w), 1840 (s, br) cm^{-1} . This reaction system when held at 65 °C (reflux) for 4 days gave a higher yield of $\text{C}_5\text{H}_5\text{Cr}(\text{H})\text{CO}[\text{P}(\text{OCH}_3)_3]_2$ (11%).

The same reaction as above was run at 25 °C for 30 min to give $\sim 40\%$ yield of $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{PO}(\text{OCH}_3)_2]\text{P}(\text{OCH}_3)_3$ and $\sim 40\%$ yield of $\text{C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ with small amounts of the hydride and the acetyl complexes.

Reaction of $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ with CO. A solution of 0.05 mmol of $\text{C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ in 0.6 mL of C_6D_6 was stirred in a CO atmosphere for 15 h. The ^1H NMR spectrum showed no trace of the methyl complex but only those for the trans acetyl complex and traces of some unidentified complex. The acetyl complex was purified by chromatography on silica gel deactivated with ether (elution with a 1:1 ether-benzene mixture). Spectral characterizations of *trans*- $\text{C}_5\text{H}_5\text{Cr}(\text{COCH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ were as follows. Mass spectrum (major ions): $\text{C}_5\text{H}_5\text{Cr}(\text{COCH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3^+$, $\text{C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3^+$, $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3^+$, $\text{C}_5\text{H}_5\text{Cr}(\text{COCH}_3)\text{P}(\text{OCH}_3)_3^+$, $\text{C}_5\text{H}_5\text{Cr}(\text{COCH}_3)\text{P}(\text{OCH}_3)_3^+$, $\text{C}_5\text{H}_5\text{Cr}(\text{CH}_3)\text{P}(\text{OCH}_3)_3^+$, $\text{C}_5\text{H}_5\text{Cr}(\text{P}(\text{OCH}_3)_3)^+$. ^1H NMR (C_6D_6 , Me_4Si): δ -4.57 (d, $J_{\text{PH}} = 2.1$ Hz, 5 H), -3.38 (d, $J_{\text{PH}} = 11.4$ Hz, 9 H), -2.86 (s, 3 H). IR (hexane): $\nu(\text{CO})$ 1940 (s), 1860 (vs), 1655 (m) cm^{-1} . Sublimation of the trans acetyl complex at 50–60 °C (0.1 mm) gave a mixture of trans and cis acetyl complex, 55 and 20%, respectively, and another acetyl complex believed to be $\text{C}_5\text{H}_5\text{Cr}(\text{COCH}_3)(\text{CO})[\text{P}(\text{OCH}_3)_3]_2$. ^1H NMR for *cis*- $\text{C}_5\text{H}_5\text{Cr}(\text{COCH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ (C_6D_6 , Me_4Si): δ -4.57 (d, $J = 2.1$ Hz, 5 H), -3.38 (d, $J = 11.4$ Hz, 9 H), -2.12 (s, 3 H). IR (hexane): $\nu(\text{CO})$ 1940 (s), 1860 (vs), 1680 (m) cm^{-1} . Results similar to those of the sublimation process were obtained by heating the trans acetyl complex in C_6D_6 at 60 °C. Ratios of trans:cis:third acetyl complex (COCH_3 ^1H resonance at δ 3.18) were $\sim 16:3:1$ after 1.5 h and $\sim 20:67:1$ after 4 h.

Solution-Phase Decomposition of $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$. A frozen solution of 0.05 mmol of $\text{C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ in 0.5 mL of C_6D_6 was sealed under vacuum in a 5-mm NMR tube. The tube was heated to ~ 76 °C for 20 h. At 25 °C, the reaction mixture was dark red and viscous. NMR analysis showed the absence of the methyl complex and the presence of (C_5H_6)₂, $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$, three acetyl complexes, and CH_4 . At 60 °C, the reaction time for complete decomposition was 8 days. With a

tetrahydrofuran solvent, the decomposition at 60 °C in 81 h was incomplete; the recovered and sublimed products were $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$ (56%) and $\text{C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ (44%).

The methane produced in a methyl complex decomposition at 80 °C (20 h) in C_6D_6 was measured in a vacuum line with a Toepler pump. The volume corresponded to 0.074 mmol of $\text{CH}_4/0.05$ mmol of initial methyl complex. The identity of the methane was confirmed by IR analysis and also mass spectrometry (theoretical m/e 16.0316, 15.0237, 14.0156; observed m/e 16.0309, 15.0233, 14.0156). A GC-MS analysis of the highly volatile organic products confirmed the presence of the cyclopentadiene dimer. Major identified organometallic products were $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$ and $\text{C}_5\text{H}_5\text{Cr}(\text{COCH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ which were recovered by chromatography and sublimed at 40–90 °C (0.1 mm).

Reaction of $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ with $\text{P}(\text{OCH}_3)_3$. A frozen solution of $\text{C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$ (0.05 mmol) and $\text{P}(\text{OCH}_3)_3$ (0.17 mmol) in 0.5 mL of tetrahydrofuran was vacuum-sealed in a 5-mm NMR tube which was then heated to 60 °C. The solution slowly discolored from bright yellow to dark yellow and finally to red-orange after 80 h. Tetrahydrofuran was vacuum removed, and the residue was sublimed at 40–90 °C (0.1 mm). NMR analysis of the residue indicated the presence of the initial methyl complex (26%), $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$ (30%), $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})[\text{P}(\text{OCH}_3)_3]_2$ (15%), $\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_2\text{P}(\text{OCH}_3)_3$ (20%), and an unidentified species with a single ^1H peak at δ 1.79. The known complexes were separated by chromatography on ether-deactivated alumina. A pure sample of $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})[\text{P}(\text{OCH}_3)_3]_2$ sublimed at 40 °C (0.1 mm) and gave the mass spectral (70 eV and 150 °C probe) ions $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})[\text{P}(\text{OCH}_3)_3]_2^+$ and $\text{C}_5\text{H}_5\text{Cr}(\text{H})[\text{P}(\text{OCH}_3)_3]_2^+$. The other hydride sublimed at 30 °C (0.1 mm) and gave the mass spectral ions (70 eV and 30 °C probe) $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3^+$ and $\text{C}_5\text{H}_5\text{Cr}(\text{H})\text{P}(\text{OCH}_3)_3^+$.

Reaction of $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$ and $[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_2]_2$ with Hydrogen. The dimers, 30 mg each, were dissolved in toluene and then exposed to a 1 atm pressure of hydrogen at 20 °C (vacuum line). After 16 h the hydrogen and the solvent were removed by evacuation. The residues were individually examined by proton NMR using toluene- d_8 . In the case of the phosphite derivative, the only detectable resonances were those of $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2\text{P}(\text{OCH}_3)_3$: δ -4.2 (d, $J = 1.2$ Hz, 5 H), -3.15 (d, $J = 12$ Hz, 9 H), +7.0 (d, $J = 90$ Hz, 1 H). For the tricarbonyl there was unreacted dimer and the hydride $\text{C}_5\text{H}_5\text{Cr}(\text{H})(\text{CO})_2$: δ -4.2 (s, 5 H), +5.65 (s, 1 H).

Crystallographic Analyses of $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$ and $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{PO}(\text{OCH}_3)_2]\text{P}(\text{OCH}_3)_3$. Single crystals of **2**, $[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{P}(\text{OCH}_3)_3]_2$, are monoclinic, space group $P2_1/c-C_{2h}^5$ with $a = 7.679$ (1) Å, $b = 17.144$ (2) Å, $c = 10.211$ (1) Å, $\beta = 112.79$ (1)°, and $Z = 2$ (dimeric species). Single crystals of **3**, $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{PO}(\text{OCH}_3)_2]\text{P}(\text{OCH}_3)_3$, are monoclinic, space group $P2_1/n$ (an alternate setting of $P2_1/c$) with $a = 7.853$ (1) Å, $b = 29.761$ (5) Å, $c = 15.203$ (2) Å, $\beta = 105.02$ (1)°, and $Z = 8$ (molecules). Three-dimensional diffraction data were collected for both compounds on a computer-controlled four-circle Syntex $P\bar{1}$ autodiffraction meter using graphite-monochromated Mo $K\alpha$ radiation and full (1° wide) ω scans. Both structures were solved using the "heavy-atom" technique. The resulting structural parameters have been refined to convergence using unit-weighted full-matrix least-squares techniques with those independent reflections (1297 for **2** and 3019 for **3**) having $2\theta(\text{Mo } K\alpha) < 43^\circ$ and $I > 3\sigma(I)$. Conventional unweighted residuals of 0.030 and 0.055 were obtained for **2** and **3**, respectively. Anisotropic thermal parameters were used for all nonhydrogen atoms in both compounds; hydrogen atoms were included with isotropic thermal parameters only for **2**. Refinement is continuing for both compounds using more extensive data sets (reflections having $2\theta(\text{Mo } K\alpha) < 63.7^\circ$ for **2** and $2\theta(\text{Mo } K\alpha) < 55^\circ$ for **3**) and more sophisticated models.

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Registry No. **1**, 12194-12-6; **2**, 68122-38-3; **3**, 54851-06-8; $\{\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}^+[\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3]^-$, 68122-40-7; *cis*- $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{CH}_3)(\text{CO})_2\text{P}(\text{OCH}_3)_3$, 68170-30-9; *trans*- $\eta^5\text{-C}_5\text{H}_5\text{Cr}$ -

(CH₃)₂(CO)₂P(OCH₃)₃, 68170-31-0; η^5 -C₅H₅Cr(H)(CO)₂P(OCH₃)₃, 68122-41-8; η^5 -C₅H₅Cr(H)(CO)[P(OCH₃)₃]₂, 60541-12-0; *cis*- η^5 -C₅H₅Cr(COCH₃)(CO)₂P(OCH₃)₃, 68170-28-5; *trans*- η^5 -C₅H₅Cr(COCH₃)(CO)₂P(OCH₃)₃, 68170-29-6.

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- (14) Cp denotes the center of gravity for the five-membered ring of the cyclopentadienyl ligand.
- (15) A complete description of the experimental conditions and structure refinement for [η^5 -C₅H₅Cr(CO)₂P(OCH₃)₃]₂, **2**, and η^5 -C₅H₅Cr(CO)₂[PO(OCH₃)₂P(OCH₃)₃], **3**, will be published in a separate paper along with detailed comparisons of the resulting parameters with those of related molecules.
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Contribution from the Departments of Chemistry, California State University, Long Beach, California 90840, and California State College, Stanislaus, Turlock, California 95380

Oxidation of Thiourea and *N,N'*-Dialkylthioureas by Hexachloroiridate(IV) Ion

HENRY N. PO,* HARUTYUN ERAN, YONGJOO KIM, and JAMES E. BYRD

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The kinetics of the oxidation of thiourea (TU), *N,N'*-dimethylthiourea (DT), and 2-imidazolidinethione (IT) by IrCl₆²⁻ in aqueous perchlorate solutions followed a third-order rate law, second order with respect to thiol concentration and first order with respect to IrCl₆²⁻. The third-order rate constants were obtained from the slopes of k_{obsd} vs. [thiol]² plots under the following reaction conditions: [IrCl₆²⁻] = 2.00 × 10⁻⁴ M, [thiol] = 1.00 × 10⁻³ to 0.015 M, pH 1.10, μ = 0.15 M, and 25.0 °C. The values of k_3 obtained are 368, 394, and 297 M⁻² s⁻¹, respectively, for TU, DT, and IT. When pH is varied from 1.10 to 4.67, a pH-rate profile is observed with constant rate at pH range 1.10–2.3 and a rapid increase in rate as the pH is raised above 2.3. The activation parameters calculated from the temperature studies (20.0–35.0 °C) yielded ΔH^\ddagger_3 = 5.76 (DT), 6.12 (TU), and 7.51 (IT) kcal mol⁻¹ and ΔS^\ddagger_3 = -27.3 (DT), -26.1 (TU), and -22.0 (IT) eu. A mechanism involving a fast preequilibrium step followed by disulfide radical formation is postulated to explain the kinetic behavior.

Introduction

The kinetics and mechanisms of oxidation of thiourea and its *N,N'*-dialkyl derivatives by different aquo complexes of metal ions¹ such as Ce(IV), Co(III), V(V), Mn(III), OsO₄, and Cu(II) and the EDTA and HEDTA complexes of Cu(II)² have been reported. In V(V), OsO₄, and Cu(II) oxidations, thiourea complexes of the metal ions have been reported. The electron-transfer mechanism that has been postulated for the metal aquo ions oxidations appeared to be inner sphere. The usual kinetics of these reactions is second order overall with an inverse dependence in [H⁺] term. Only the EDTA and HEDTA complexes of Cu(II) show second-order dependence in thiourea.

Recently, Hoffmann and Edwards³ have reported the reaction mechanism for the oxidation of thiourea and its *N,N'*-dialkyl derivatives by hydrogen peroxide. The mechanism they have postulated involves an activated complex of hydrogen peroxide and thiourea. This has been postulated to explain the large negative entropy of activation observed in these reactions.

In this paper we report the results of a study of the oxidation of thiourea (TU), *N,N'*-dimethylthiourea (DT), and 2-imidazolidinethione (IT) (E° = -0.42 to -0.46 V⁴) to the corresponding disulfide compounds by the outer-sphere oxidant, IrCl₆²⁻ (E° = 1.02 V).⁵ This oxidant has been chosen

to circumvent the substitution rate-controlled reaction when metal aquo ions are used.

Experimental Section

Reagents. Thiourea (TU), *N,N'*-dimethylthiourea (DT), and 2-imidazolidinethione (IT) were obtained from Aldrich Chemical Co. Thiourea and 2-imidazolidinethione were extensively recrystallized from ethanol-water solution and DT was repeatedly recrystallized from dioxane solution until clear white crystals were obtained. All of the recrystallized compounds were dried under vacuum. The purities of the recrystallized compounds were checked by comparing the melting points and NMR and UV spectra with those from literature and Aldrich Spectra Handbook.

Sodium perchlorate solution was prepared by neutralizing anhydrous sodium carbonate with 70% perchloric acid. The concentration of sodium perchlorate was analyzed gravimetrically. The water used in the experiments was purified by passing through two ion-exchange columns and redistilled using an all-glass apparatus.

Potassium hexachloroiridate(IV) was obtained from Alfa Products (Ventron) and used without further purification.

Stoichiometry and Product Studies. The reaction stoichiometry for the oxidation of TU, DT, and IT was obtained using the following procedure. Excess IrCl₆²⁻ was reacted with the reducing agents and the change in absorbance at 488 nm was used to determine the amount of IrCl₆²⁻ consumed. In all three systems, a variable stoichiometry was obtained depending on the initial concentration ratios of IrCl₆²⁻ and the reducing agents, Figure 1. The stoichiometry varies from 1 to approximately 6 depending on the initial concentration ratio of the reactants. At no time was an 8:1 stoichiometry observed as

* To whom correspondence should be addressed at California State University.