# Synthesis and Reactions of η-Cyclopentadienylhydridotris(trimethyl phosphite)chromium(II)

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*Summary* The synthesis and physical characteristics of a novel chromium hydride, $[(\eta\text{-}C_5H_5)Cr\{P(OMe)_3\}_3H]$, (I), are described; several reactions of this compound, including exchange of $CH_3O$-groups with $CD_3O$, $P(OMe)_3$ with CO and NO, and Cr–H with $D_2$ are reported.

TRANSITION metal hydrides stabilized by $\pi$-acceptor ligand molecules are of general interest as potential participants in homogeneous catalysis. We report an example of such a system containing the cpCr species (cp = $\eta$-cyclopentadienyl). When a tetrahydrofuran (THF) solution of $cpCrCl_2{\cdot}THF$ is treated with a 2—3-fold excess of $NaBH_4$, the presence of hydride species in the reaction product is indicated by mass spectrometry with peaks corresponding, among others, to $cpCrH_2{\cdot}THF$ and $cpCr(BH_4)_2$. While substances with defined composition could not be isolated from these reaction mixtures, a stable hydride complex, $\eta$-cyclopentadienylhydridotris(trimethyl phosphite)chromium(II) (I), is obtained as air-sensitive yellow flakes in almost quantitative yield, when this reaction is carried out in the presence of an excess of $P(OMe)_3$.

Compound (I) decomposes without melting above 160 °C. However, it can be sublimed under high vacum at 50—60 °C with partial decomposition. It is freely soluble in polar and non-polar organic solvents. In the absence of air, these solutions are reasonably stable. The deuterium analogue of (I) is prepared in the same way, using $NaBD_4$. The mass spectrum of (I), $m/e$ 490 ($M^+$), 366 $[cpCr\{P(OMe)_3\}_2\text{–}H]^+$, 365 $[cpCr\{P(OMe)_3\}_2]^+$, 242 $[cpCr\{P(OMe)_3\}H]^+$, and 241 $[cpCrP(OMe)_3]^+$, is fully compatible with the proposed composition $[cpCr\{P(OMe)_3\}_3H]$; one of the phosphite ligands is more readily eliminated than the hydrogen bound to the metal. The $^1H$ n.m.r. spectrum of (I) shows the hydride proton as a symmetrical 1:3:3:1 quartet at $\tau$ 19·70 ($J_{P\text{–}H}$ 75 Hz). This splitting undoubtedly arises from the three magnetically equivalent phosphorus atoms. The cyclopentadienyl protons at $\tau$ 5·54 are similarly split into a quartet by the three phosphorus atoms ($J_{P\text{–}H}$ 1·5 Hz). The equivalence of the phosphorus atoms is confirmed by the $^{31}P$ n.m.r. spectrum. In the proton-decoupled phosphorus spectrum only one singlet appears. For this signal, one observes a high-field shift compared to the uncomplexed ligand (co-ordination shift +31·15 p.p.m.); similar high-field co-ordination shifts have been reported earlier, particularly for co-ordination compounds containing metals in positive oxidation states.[1,2] Without decoupling, the phosphorus resonance is split into a doublet with $J_{P\text{–}H}$ 75 Hz, in accord with the splitting observed for the metal hydride. Splitting by the nine MeO protons is presumably hidden under a line width of 20—25 Hz. The MeO protons resonance appears as an irregular quartet[3] with an apparent splitting of 3 Hz.

A trigonal bipyramidal arrangement of the ligands with the hydrogen atom *trans* to the cyclopentadienyl ring would be the only conceivable non-fluxional structure consistent with these spectral data, particularly with the observed equivalence of all three phosphorus atoms. Similar axial structures are known, in particular for $[CoH(N)_2(PPh_3)_3]$[4] and $[RhH(CO)(PPh_3)_3]$.[5] On the other hand, a non-axial structure with phosphite and hydride ligands at the base of an approximate square pyramid would be equally compatible with these spectral data, if a fast pseudorotation exchanges the phosphite groups *cis* and *trans* to the hydride ligand. Similar fluxional behaviour has been observed for the analogous complexes $[CpW(CO)_3H]$[6] and $[CpMo(CO)_2\text{-}PR_3H]$[7] by variable-temperature n.m.r. spectroscopy. In the case of (I), however, no significant changes in the n.m.r. spectra are observed at *ca.* −110 °C. We must therefore conclude that in all likelihood the observed equivalence of the three phosphite ligands is not due to a stereochemical non-rigidity, but rather due to their trigonally symmetric arrangement in (I).

Although M–H stretching vibrations are unique for complex metal hydrides, the i.r. spectrum of (I) shows no clearly defined absorption in the region 2500—1600 $cm^{-1}$ attributable to the Cr–H bond. Interestingly, a similar observation was reported for the related structures [cpCr(CO)$_3$H][8] and [HCo(PX)$_3$)$_4$].[9,10]

Upon treatment with $CCl_4$, (I) is reconverted into cpCrCl$_2$·P(OMe)$_3$. Ligand exchange of (I) occurs with CO at 1 atm; after 3—4 days one obtains a near-quantitative yield of a monocarbonyl compound, [cpCr{P(OMe)$_3$}$_2$(CO)H], $\nu$(CO) 1840 $cm^{-1}$, *m/e* 394 ($M^+$), $\tau$ 18·61 (1H, t, $J_{P-H}$ 39 Hz, Cr–H). Reaction of (I) with a limited amount of NO yields, within 2 h, the nitrosyl complex [cpCr{P(OR)$_3$}$_2$NO], identified by its $^1H$ n.m.r. spectrum with the expected $C_5H_5$ triplet and OMe signal (ratio 1 : 3·6), a strong i.r. band at 1625 $cm^{-1}$ $\nu$(NO), and *m/e* 395 ($M^+$). Excess of NO yields, as the sole product, an olive green sublimable material which was tentatively assigned the structure [{cpCr(NO)$_2$}$_3$-H] on the basis of its spectroscopic data: *m/e* 532, $^1H$ n.m.r. spectrum with a single, sharp $C_5H_5$ signal, and $\nu$(NO) 1705 and 1810 $cm^{-1}$.[11] Ligand exchange thus appears to be a fairly ready reaction mode for [cpCr{P(OR)$_3$}$_3$H]. Anion formation by proton abstraction from the M–H group could not be observed with basic reagents such as $NaNH_2$ or Na alkoxides; instead, attack at the phosphite ligands appears to be preferred. Treatment with $CD_3ONa$ in $CD_3OD$ resulted in exchange of 1—9 MeO groups with $CD_3O$ groups during 24 h, while little, if any, Cr–H was converted into Cr–D. Reaction with 1 mol. equiv. of methyl-lithium in THF gave [cpCr{P(OR)$_3$}$_2$PMe$_3$H] in small quantities.

In contrast to its inertness to basic reagents, a fairly ready exchange of the metal hydride with $D_2$ can be observed by mass spectrometry. When exposed to 1 atm of $D_2$ in light petroleum or THF solution for 4—8 days at room temperature, $> 50\%$ of the hydride is converted into [cpCr{P(OMe)$_3$}$_3$D]. This reaction does not occur with [($\eta$-$C_5H_5$)Mo(CO)$_3$H][12] at room temperature. Presumably intermediate dissociation of a phosphite ligand to yield a co-ordinatively unsaturated intermediate capable of oxidative addition of $D_2$ occurs more easily than that of a CO ligand.

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