Table VI. Magnetic Moments[a] of Chloromolybdenum Complexes

$Mo(dcq)_3Cl$	2.71 (2.39)	$Mo(dcq)_2Cl_2$	2.62 (2.42)
$Mo(pic)_3Cl$	2.70	$Mo(cq)_2Cl_2$	2.78
$Mo(nq)_3Cl$	1.87	$Mo(q)_2Cl_2$	2.53

[a] Magnetic moments in Bohr magnetons at 294 K with selected values in parentheses for 77 K.

is somewhat different from those of the other MoL_3Cl complexes studied; cf. infrared spectral section above.

Conductivity Measurements. These measurements were very difficult to obtain due to the tendency of $Mo(dcq)_3Cl$ to oxidize in polar solvents. However, the data in Table V indicate that the $Mo(dcq)_3Cl$ complex is completely dissociated and acts as a one-to-one electrolyte just like KI; however, as the polarity decreases, the degree of ion pairing increases at a greater rate than that of KI, even though the large complex ion should not attract chloride that well by electrostatic considerations. This suggests that the molybdenum species is a six-coordinate $Mo(dcq)_3^+$ complex in polar solvents and is a seven-coordinate species with coordinated chloride in nonpolar solvents. Two seven-coordinate monochloro complexes of tungsten(II) show analogous behavior.[19] Unfortunately, solubility and stability considerations do not allow measurements a wider range of polarities.

Magnetic Moments. The magnetic moments for all of the complexes are slightly below the spin-only value for a d^2 system because of spin–orbit coupling (Table VI) and are consistent with the moments obtained for MoL_2Cl_2 complexes[1] and also that obtained for $Mo[S_2P(OR)_2]_3Cl$.[5] The magnetic moment of 2.53 μ_B for $Mo(q)_2Cl_2$ is within experimental error of the 2.58 μ_B value reported by the Australian workers for this complex.[1]

Although Moss and Shaw[17] were able to correlate magnetic moment with coordination number for six-coordinate *trans*-$WCl_4(PMe_2Ph)_2$ and seven-coordinate $WCl_4(PMe_2Ph)_3$, for the complexes in this study it was not possible to clearly distinguish between the six- and seven-coordinate complexes on the basis of magnetic properties. The moments for all of the complexes, with the exception of $Mo(nq)_3Cl$, lie between 2.5 and 2.8 μ_B, and the magnetic moments of $Mo(dcq)_3Cl$ and $Mo(dcq)_2Cl_2$ show similar temperature dependence. The complexes are of such low symmetry that arguments based on ground-state symmetry[17,18] for the complexes are not valid.

The magnetic moment of $Mo(nq)_3Cl$ is anomalous. The moment is below that of other spin-free Mo(IV) complexes. This observation, combined with the lack of any observable terminal Mo–Cl stretching vibration in the solid-state infrared spectrum and the solvent dependence of the electronic spectra, provides evidence that the monomeric seven-coordinate complex exists in chloroform and dimerizes to a chlorine-bridged eight-coordinate species in the solid state and in toluene. Proof of such a structure, however, awaits a more detailed study.

Acknowledgment. We acknowledge with gratitude the National Science Foundation Materials Research Laboratory at the University of Massachusetts, a Dow Fellowship to C. J. Weber, and the Army Research Office for support of this work and Climax Molybdenum for some of the $MoCl_4$ and $MoCl_5$ used in this study. We also appreciate the constructive suggestions made by reviewers of the original manuscript.

Registry No. $Mo(q)_2Cl_2$, 36470-65-2; $Mo(cq)_2Cl_2$, 87739-28-4; $Mo(dcq)_2Cl_2$, 74594-57-3; $Mo(dsp)Cl_2$, 87739-29-5; $Mo(dcq)_3Cl$, 74620-90-9; $Mo(pic)_3Cl$, 87739-32-0; $Mo(dcq)_4$, 87739-33-1; $Mo(dbq)_3Cl$, 87739-31-9; $Mo(nq)_3Cl$, 87739-30-8.

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Electronic Effects on the Orientation of H_2 Addition to an Iridium(I) Complex

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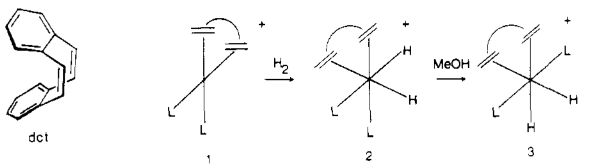
Hydrogen addition to d^8 metal complexes is an important step in hydrogenation and hydroformylation catalysis. We studied the factors that determine which of several possible isomers is formed on H_2 addition to Ir(I) complexes. This might influence the course of catalysis in asymmetric hydrogenation,[2] for example.

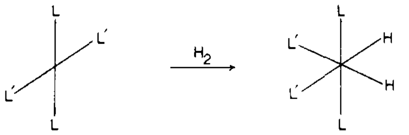
In a concerted addition, the two hydrides would normally be expected to occupy mutually cis positions in the product. A possible counterexample[3] has now been satisfactorily rationalized on the basis of cis addition.[4]

When several isomers having cis hydrides are possible, it is not always the thermodynamically most stable isomer that is formed. For example, we have shown that $[(dct)IrL_2]BF_4$

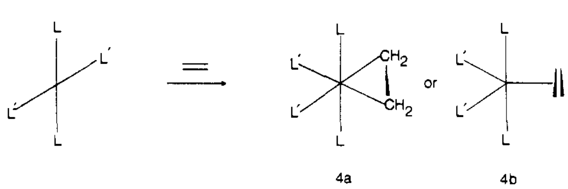


(1)

(**1**: dct = dibenzo[*a*,*e*]cyclooctatetraene; L = PPh_3) adds H_2 to give a cis dihydride (**2**) in CH_2Cl_2 at −30 °C, but on addition of a trace of a weak base (e.g., MeOH), this isomer rearranges by a deprotonation/reprotonation mechanism to give the thermodynamically more stable cis,trans isomer (**3**).[5] This has mutually cis hydrides but cannot be formed from **1** directly if only processes of the type shown in eq 2 are invoked. An analogy can be seen to exist between the H_2 addition process of eq 2 and the addition of a simple 2-electron donor such as an olefin (eq 3) to give **4**. In each case, two trans ligands L′ fold back as the incoming 2-electron donor H_2 or C_2H_4 approaches. The olefin adduct could be considered a 6-coordinate M(III) (**4a**) complex or a 5-coordinate M(I) complex (**4b**). Structure **4a**,[6] the metallacyclopropane model, makes the analogy with the dihydride clearer.



(2)



(3)

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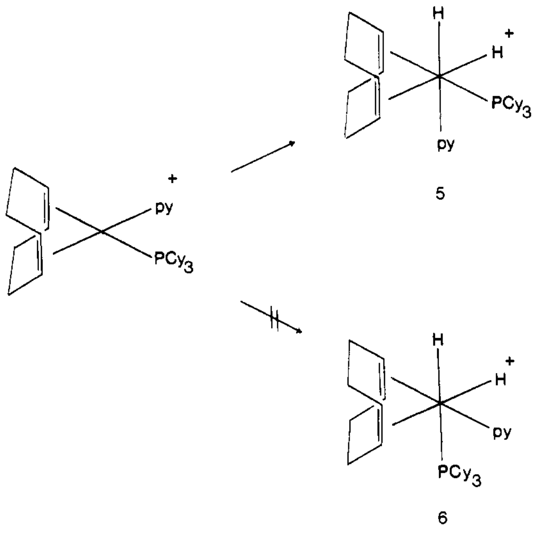
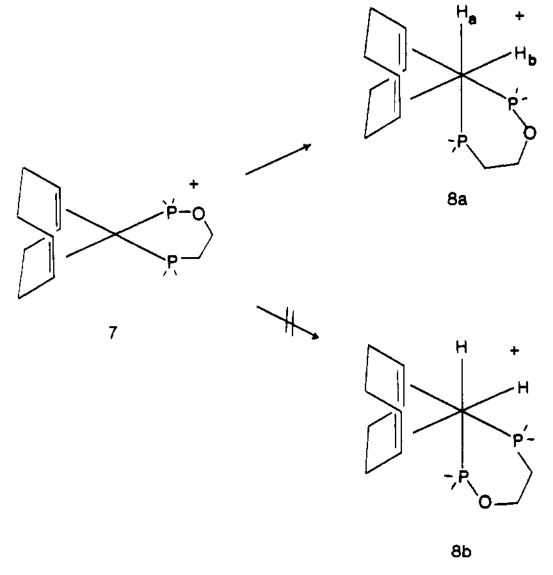
In our studies[7] on H_2 addition to [Ir(cod)(PCy$_3$)(py)] (cod = 1,5-cyclooctadiene; Cy = cyclohexyl; py = pyridine) we found that H_2 addition took place to give only isomer **5**. No subsequent rearrangement took place. The most straightforward explanation for this is to imagine that *5* is both the kinetically and thermodynamically most stable product. It is striking that the presence of the pyridine ligand can completely orient H_2 addition to give **5** and not **6** although either could be formed via the route of eq 2. It is clear that either a steric effect, an electronic effect, or both effects are at work. We were particularly interested to determine if an electronic effect were present; thus, we studied a case in which the steric effect would be negligible. In the case of the chelating ligand Ph$_2$POCH$_2$CH$_2$PPh$_2$ (pop), we expect the steric effects at each phosphorus terminus to be insignificantly different, yet the electronic character will differ substantially.



(4)

pop was prepared by the literature route[8] and was found to react with [Ir(cod)Cl]$_2$ and AgBF$_4$ in CH$_2$Cl$_2$ to give [Ir(cod)(pop)]BF$_4$ in good yield. This complex was assigned structure **7** on the basis of analytical and spectral data. In particular, the ^{31}P NMR spectrum showed two doublets at +102.5 and +2.8 ppm (relative to 85% H$_3$PO$_4$), respectively, with a mutual coupling of 32 Hz. In the free ligand the coupling is undetectable, so the coupling observed in pop complexes seems to be due to coupling via the metal.[8] On addition of H_2 to a CD$_2$Cl$_2$ solution of [Ir(cod)(pop)]BF$_4$ at −80 °C, only one isomeric dihydride is formed in quantitative yield as shown by the proton NMR spectrum. In this adduct, H$_a$ resonates at −10.18 ppm (dd, ^2J(P,H) = 21.5, 80.5 Hz) and H$_b$ at −12.90 ppm (dd, ^2J(P,H) = 19.8 Hz).



(5)

Table I. ^{1}H and ^{31}P NMR Data

compd	^{31}P NMR	^{1}H NMR[a]
Ph$_2$P$_a$OCH$_2$CH$_2$P$_b$Ph$_2$[d]	+111, s, P$_a$ −22, s, P$_b$	7.3, c, Ph 2.5, 4.0, c, CH$_2$
[Ir(cod)(pop)]BF$_4$ (7)	+102.5, d (32), P$_a$ +2.8, d (32), P$_b$	7.3, c, Ph 2.7, 4.1, c, pop CH$_2$ 1.9, c, cod CH$_2$ 4.3, c, cod CH
[IrH$_2$(cod)(pop)]BF$_4$ (8a)	+75, c, P$_a$ −15, c, P$_b$	−10.18, dd (21.5,[b] 80.5[c]), H$_a$ −12.9, t (19.8), H$_b$ 1.9, c, cod CH$_2$ 4.5, c, cod CH 4.2, 2.9, c, pop CH$_2$

[a] Reported as position (ppm relative to Me$_4$Si or 85% H$_3$PO$_4$; negative values upfield), multiplicity (*J*, Hz), assignment. [b] Coupling to P$_a$ determined by selective ^{31}P decoupling. [c] Coupling to P$_b$ determined by selective ^{31}P decoupling. [d] Reference 8.

When the mixture is warmed to room temperature, no changes occur until +5 °C where the coordinated H_2 begins to transfer to the coordinated cod to give cyclooctene and undefined iridium-containing species, probably metal clusters.[9] No rearrangement of **8a** to another isomer is ever observed.

The configuration of **8a** was determined by ^{31}P decoupling of the ^{1}H spectrum of **8a**. This work relies on the correct identification of P$_a$ and P$_b$ in the ^{31}P NMR spectrum.

The chemical shifts of the two phosphorus nuclei in **8a** appear at +75 ppm (P$_a$) and −15 ppm (P$_b$). Each falls into a range[10] characteristic for phosphinite and tertiary phosphine complexes, respectively, and leads to the assignment of P$_a$ to the Ph$_2$POR group and P$_b$ to the Ph$_2$PR group. We find that decoupling of P$_b$ leads to the disappearance only of the trans ^2J(P$_b$,H$_a$) coupling and the cis ^2J(P$_b$,H$_b$) coupling in the ^{1}H NMR spectrum, showing that configuration **8a** is the correct one. This is confirmed by decoupling P$_a$, in which case the cis couplings to H$_a$ and H$_b$ disppear. Table I gives the detailed analysis of the spectra in each case.

An unusual feature of the low-temperature ^{1}H NMR spectra of **8a** is the appearance of a second set of hydride peaks, never amounting to more than 15% of the integrated intensity. These are identical in splitting pattern with the major peaks but slightly displaced. Increasing the temperature leads to a reversible diminution in the integrated intensity of these peaks, and we ascribe them to two closely related conformers, possibly differing in the conformation of the PPh$_2$ groups or the OCH$_2$CH$_2$ chain.

We imagine that the transition state leading to **8a**, shown as **9a**, is lower in energy by at least a few kilocalories compared to the transition state **9b**, which leads to **8b**. Several factors may favor **9a** over **9b**. To discuss these we shall regard **9a** as a 5-coordinate trigonal-bipyramidal H_2 adduct of [Ir(cod)(pop)]$^+$. This requires H_2 to be a simple 2-electron donor like C_2H_4. The orbitals available for interaction with the metal (**9a** and **9b**) are indeed similar in the two systems, and the

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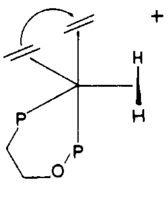
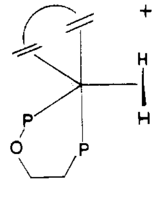


9a



9b

rotamer shown in **9a**, with both H atoms in the equatorial plane, should be favored, as is known to be the case for olefins.[11] In the case of olefins, the π^* orbital of the ligand can orient the olefin, but in the case of H_2, it is proposed that the σ^* orbital plays an analogous role. It can be seen that the equatorial cod C=C group and the H_2 molecule share d orbitals with Ph_2PR in **9a** but with the better π-acceptor Ph_2POR in **9b**. The former is preferred, as discussed for the case of olefins by Hoffmann et al.[12] A further advantage of **9a** is the presence of the more electronegative Ph_2POR group in the axial rather than the equatorial position, which is known to be preferred.[13]

It should be noted that **9a** may be an intermediate with free rotation of the H_2 around the M-H_2 axis, rather than a transition state, in view of the recent isolation of an η^2-H_2 complex, $[W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)]$.[14] As expected on the basis of the ideas presented above (but not on simple steric grounds), the orientation of the H_2 molecule in the tungsten complex is approximately parallel with the P-W-P axis, as shown by neutron diffraction.[15]

The formation of the product shown in eq 4 is also consistent with this idea since pyridine seems to be slightly more electron donating than PCy_3,[16] but as previously mentioned, this reaction could be easily under steric control.

We conclude that the addition of H_2 to a metal complex can be directed by the electronic effect of the ligands. We propose that the σ and σ^* orbitals of H_2 can play the same role as the π and π^* orbitals of olefins in orienting the molecule on the metal and that arguments[12] successfully applied to olefins can be extended to cover the case of H_2. It would have been interesting to compare these results with those for olefin addition to the same complex. Unfortunately, there was no reaction between $[Ir(cod)(L_2)]^+$ and maleic anhydride or TCNE. We have rationalized the observed direction of addition in terms of competition for metal d electrons in a proposed trigonal-bipyramidal transition state. Clearly, further examples are required before the generality of these ideas can be completely assessed.

Experimental Section

All complexes were prepared by using standard inert-atmosphere, Schlenk tube techniques. CH_2Cl_2 was distilled from CaH_2 and Et_2O from Na/Ph_2CO before use. ^1H NMR spectra were recorded on a Brucker 270-MHz instrument and ^{31}P NMR spectra on a Varian CFT-20.

(Diphenylphosphino)ethyl diphenylphosphinite (pop) was prepared by the method of ref 8, except that the product was chromatographed on alumina with benzene as eluent and stored as a standard solution in benzene under N_2. The ^{31}P NMR spectrum of the product was identical with that reported in ref 8.

(1,5-Cyclooctadiene)((diphenylphosphino)ethyl diphenylphosphinite)iridium(I) Tetrafluoroborate. To a solution of $[Ir(cod)(MeCN)_2]BF_4$ (0.47 g, 1 mmol) in CH_2Cl_2 (20 mL) at -78 °C was added dropwise pop (1 mmol) in benzene (5 mL). The red solution was stirred at -78 °C (30 min) and then at room temperature (1 h). The volume of the solution was reduced to 5 mL in vacuo and the product isolated with Et_2O, washed with Et_2O, and dried in vacuo. Anal. Calcd for $C_{34}H_{36}IrP_2OF_4B\cdot{}^1/_2CH_2Cl_2$: C, 49.07; H, 4.42; P, 7.34. Found: C, 48.99; H, 4.80; P, 7.45.

Dihydrido(1,5-cyclooctadiene)((diphenylphosphino)ethyl diphenylphosphinite)iridium(III) Tetrafluoroborate. A solution of $[Ir(cod)(pop)]BF_4$ in dichloromethane (for ^1H NMR, 30 mg in 0.4 mL of CD_2Cl_2; for ^{31}P NMR, 100 mg in 1.5 mL of CH_2Cl_2) was treated with H_2, and the spectra observed in Table I were observed. The configuration was determined as **8a** by ^{31}P decoupling the ^1H spectrum and using frequencies determined in the ^{31}P NMR experiment.

Registry No. 7, 87556-62-5; **8**, 87567-00-8; pop, 32309-62-9; H_2, 1333-74-0.

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Mechanical Spectroscopy of Organometallic Complexes: Assignment of the Spectrum of $C_6H_6Cr(CO)_3$ to Ring Rotation

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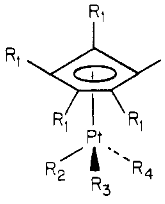
Recently we reported preliminary studies[1] of the mechanical spectra of six cyclopentadienylplatinum(IV) alkyl complexes of the type $CpPtR_1R_2R_3$ (**1-6**), where $R_1R_2R_3$ were combinations of methyl, ethyl, and acyl groups. The experiments[2,3] consisted of subjecting a rigid piece of polystyrene,[4] in which the complex was dissolved, to a mechanical displacement and allowing it to return to its rest position. The damping of the resultant vibration is dependent upon the degree to which the energy imparted by the initial displacement is dissipated. If the molecules of the sample undergo molecular motion(s) that can interact with the mechanical motion of the matrix, then it may be possible to bring the two into resonance. This was achieved by varying the temperature of the sample (thus changing the molecular dynamics) and keeping the frequency of the mechanical motion approximately constant. Resonance causes an increase in the rate of damping and results in a peak in the $\tan \delta^1$ vs. temperature plot. The presence of a platinum complex gave a peak in the spectrum, at a temperature that depended upon the set of alkyl ligands in the $PtR_1R_2R_3$ tripod.



1: $R_1 = H, R_2 = R_3 = R_4 = CH_3$
2: $R_1 = H, R_2 = R_3 = CH_3, R_4 = C(O)CH_3$
3: $R_1 = H, R_2 = R_3 = C_2H_5, R_4 = C(O)CH_3$
4: $R_1 = H, R_2 = R_3 = C_2H_5, R_4 = CH_3$
5: $R_1 = H, R_2 = CH_3, R_3 = C_2H_5, R_4 = C(O)CH_3$
6: $R_1 = C_6H_5, R_2 = R_4 = CH_3$

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