National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 8714258) for funds for the purchase of the NMR spectrometers. We are most grateful to Professor T. J. Smith (Kalamazoo College, MI) for the use of his Perkin-Elmer 330 UV/VIS/NIR spectrophotometer.

Supplementary Material Available: Listings of positional parameters and their errors for the phenyl carbon atoms of **1**, **2**, and **3**, the lattice solvent molecules of **1** and **3**, and the PF_6^- atoms of **3** (Tables S1, S2, and S3), thermal parameters (Tables S4, S5, and S6), complete listings of bond distances (Tables S7, S8, and S9) and bond angles (Tables S10, S11, and S12), electronic absorption spectral data for representative complexes of the type *cis*- and *trans*-$[Re_2(O_2CR)_2X_2(dppm)_2]^{0,+}$ (Table S13), and figures showing the full atomic numbering schemes for **2** and **3** (Figures S1 and S2) (29 pages); tables of observed and calculated structure factors (57 pages). Ordering information is given on any current masthead page.

The Origin of the Directing Effect in H_2 Addition to Square-Planar d^8 Complexes

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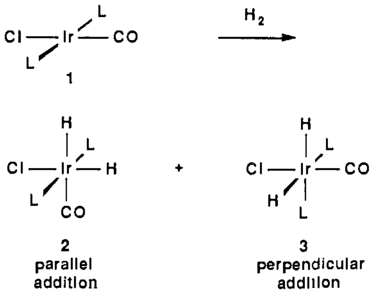
Abstract: Hydrogen adds to square-planar d^8 complexes of the Vaska type [*trans*-$IrX(CO)(PR_3)_2$] to give oxidative addition products in which the H_2 has added parallel to the X–Ir–CO axis. In principle, however, addition perpendicular to this axis should also be possible. Three models have been discussed to account for the apparent preference for parallel adducts. We show that in contrast to the chloro complex (X = Cl, parallel adduct formed), the methyl, phenyl, or hydride analogues give perpendicular adducts. In one case (X = Ph), the perpendicular adduct is formed at –80 °C, but rearranges to the parallel adduct on warming via reductive elimination of H_2 and readdition. These findings seem to invalidate the previous theoretical models that have been proposed to explain the direction of H_2 addition. A new one is suggested that covers all the data gathered up to now.

Hydrogen may in principle add in one of two ways to a square-planar d^8 complex, as shown in eq 1 for the case of Vaskas complex (**1**). The two H ligands are cis to one another in both products, as expected from a concerted process, but in one case (**2**) H_2 is trans to Cl and CO, and in the other (**3**) H_2 is trans to the PPh_3 groups. For the parent complex (X = Cl), only the parallel adduct, **2**, is observed.



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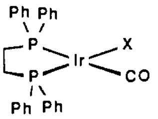
In the formation of **2** and **3**, the H_2 has added parallel and perpendicular, respectively, to the Cl–Ir–CO symmetry axis. We shall therefore refer to **2** and **3** as the "parallel" and "perpendicular" adducts. In cases such as **4** in which neither of the two directions is coincident with an axis of symmetry of the molecule, we will choose an axis and indicate the choice in parentheses, e.g., parallel (CO) means parallel to the M–CO bond. Understanding the factors that determine which isomers are formed is a fundamental problem and may also be of help in rationalizing the course of asymmetric hydrogenation and other catalytic reactions.

Eisenberg et al.[1] have found that the parallel (CO) adducts are the kinetic products in the addition of H_2 to **4** (X = Cl, Br, I, CN), and they discussed two possible reasons. One proposal involves increased overlap of $\sigma^*(H_2)$ with the $d_\pi(M)$ orbital through the involvement of $\pi^*(CO)$ in the transition state. This picture predicts that addition should always take place parallel to the best π-acceptor ligand (i.e., CO in **4**, as observed). It also explains the formation of parallel adducts in H_2 addition to **1**, and was consistent with most of the available data known at the time it was proposed. This model requires a transition state[1e] closely resembling the square-planar starting material and unlike the trigonal-bipyramidal transition state of type **6** that we invoked.



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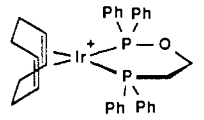

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In an alternative model, first suggested by Wolczanski and also considered by Eisenberg et al.,[1] addition should occur parallel to the highest trans effect ligand (see eq 9 and 10 and further discussion below).

We reported in 1983 that H_2 addition to **5** gave the perpendicular (P–O) adduct **7a**.[2a] In contrast, the parallel (P–O) adduct **7b** would be expected on the basis of the ideas subsequently developed by Eisenberg et al.,[1] since the Ph_2PO group is the better π-acceptor. We had proposed a different picture: that stereochemical preferences within a trigonal-bipyramidal transition state (or intermediate) of type **6** is the critical factor in deciding which isomer is formed. For example, in eq 2 we postulated that **7a** is formed rather than **7b** because **6a** is stabler than **6b**. Several useful theoretical studies of H_2 addition are available.[3a]

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(1) (a) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148–60. (b) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772–4. (c) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531–40. (d) Kunin, A. J.; Farid, R.; Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 5315–7. (e) Eisenberg et al.[1d] have evidence that the transition state is not late.

(2) (a) Crabtree, R. H.; Uriarte, R. J. *Inorg. Chem.* **1983**, *22*, 4152–54. (b) Burk, M. J.; Crabtree, R. H. *Inorg. Chem.* **1986**, *25*, 931–2.

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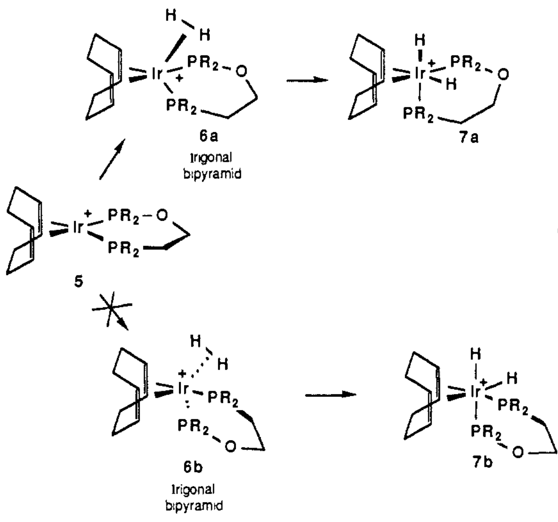


(2)

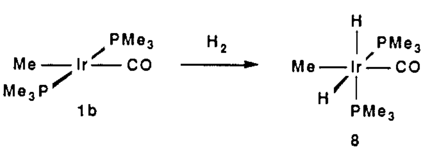
The purpose of this paper is to report the result of experiments designed to test these and one other unpublished model for predicting the direction of H_2 attack. We now believe that all three models are flawed, and so propose a new one that rationalizes all the cases studied to date.

Results and Discussion

We recently reported a good synthetic route to $[IrCl(CO)(PMe_3)_2]$ (**1a**)[2a] and, in connection with some alkane activation experiments, made the corresponding methyl complex **1b** $[IrMe(CO)(PMe_3)_2]$ by the route shown in eq 3, followed by sublimation. The methyl complex **1b** has also been reported by Bennett et al.,[4] who made it in a similar way.

$$\underset{\mathbf{1a}}{IrCl(CO)(PMe_3)_2} \xrightarrow{LiMe} \underset{\mathbf{1b}}{IrMe(CO)(PMe_3)_2} \qquad (3)$$

The Direction of H_2 Addition. Our interest[2] in the H_2 addition problem led us to determine the stereochemistry of H_2 addition to **1b**. In contrast to all other complexes of the Vaska type studied to date, the perpendicular adduct **8** was formed, even at -80 °C.



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The adduct **8** is remarkable in having a methyl group cis to two hydride ligands. A number of related cases are known[5a-c] in which cis alkyl hydride complexes have been found in the (trimethylphosphine)iridium(III) system. It has been suggested that the kinetic stability of such complexes is due to their coordinative inertness, the small and tightly bound PMe_3 group being less easily lost than are larger ligands, such as PPh_3. The corresponding PPh_3 analogue of **8** loses CH_4 at -40 °C.[6] Theoretical studies[3b] have rationalized faster reductive elimination in a 16e than an 18e d^6 species.

The stereochemistry of **8** is clearly defined by the ^1H NMR spectrum. In particular, a doublet at δ 1.14 ($^2J(P,H) = 7.7$ Hz) is assigned to the PMe_3 groups. The lack of virtual coupling shows these groups are cis. A complex resonance at δ -10.05 is assigned to the Ir-H groups split in an AA′XX′ pattern with trans phosphorus ($J(P,H \text{ trans}) = 130$ Hz) as well as by the Ir-CH_3 protons. The methyl group resonates as a triplet ($^3J(P,H) = 12$ Hz) of triplets ($^3J(H,H) = 1.8$ Hz) which can be assigned to the Ir-CH_3 group split by two cis-phosphorus and two cis Ir-H nuclei.

Table I. Direction of Addition to Vaskas Complex

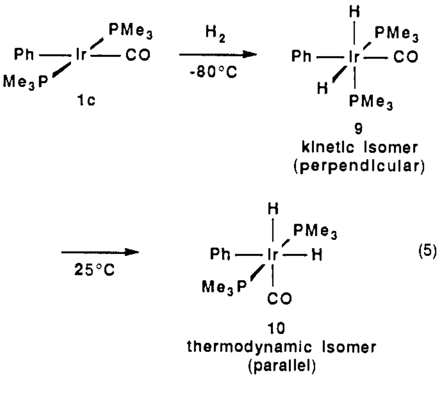
	parallel	perpendicular[a]
$IrClCO(PMe_3)_2$ (**1a**)	H_2, CO	
$IrMeCO(PMe_3)_2$ (**1b**)	PMe_3	H_2, C_2H_4, MA
$IrPhCO(PMe_3)_2$ (**1c**)	H_2 (therm)	H_2 (kinetic)
$IrClCO(PPh_3)_2$	H_2, CO[13]	
$IrBrCO(PPh_3)_2$	H_2[13]	TCNE[16]
$IrHCO(PPh_3)_2$		D_2,[17] $SiPh_3H$[18] FMN[11]
$IrMe(CO)(PPh_3)_2$		H_2[5b,12]

[a] MA = maleic anhydride, FMN = fumaronitrile.

The perpendicular adduct is certainly formed from **1b**, but is it the kinetic product? Conceivably, H_2 might have added to give the parallel adduct, which then rapidly rearranges. We were able to exclude this possibility for the case of the phenyl complex $[Ir(Ph)(CO)(PMe_3)_2]$ (**1c**) synthesized by the route of eq 3 but with PhLi. **1c** is completely converted to the perpendicular adduct **9** by reaction with H_2 at -80 °C. At 25 °C, this adduct undergoes a first-order rearrangement to give the parallel adduct **10** with a $t_{1/2}$ of 10 min at 25 °C.

The identities of **9** and **10** follow from the ^1H NMR spectrum. In particular, **9** shows an AA′XX′ Ir-H resonance pattern at δ -9.78 similar to that of the Ir-Me analogue **8**, with a $^2J(P,H \text{ trans})$ of 135 Hz. The PMe resonance is a simple doublet ($^2J(P,H) = 8.3$ Hz) at δ 1.13, showing no sign of virtual coupling. In contrast **10** shows two Ir-H resonances, one at δ -9.22 and the other at δ -12.2. These are mutually coupled, and the value of $^2J(H,H)$, 5.3 Hz, is fully consistent with a classical dihydride structure as expected for H_2 addition to a d^8 species, and also proves that inequivalent Ir-H groups are present in the same complex. The PMe resonance at δ 1.24 is virtually coupled ($J_{app} = 3.8$ Hz), showing that these groups are mutually trans.

Two mechanisms (eq 6 and 7) for the isomerization of **9** to **10** seem most reasonable. The first involves reductive elimination and re-addition of Ph-H. Since the solvent is C_6D_6 and no deuterium appears in **10**, any such mechanism would require an η^2-C_6H_6 intermediate, as proposed by Jones and Feher[7a] in a related system. We were able to rule out this process by studying the D_2 adduct of **9**. This should give an η^2-C_6H_5D complex that on re-addition to the metal should lead to the incorporation of deuterium into the Ir-Ph group, and of protium into the Ir-H groups of **10**. This is not observed: d_2-**9** gives d_2-**10** with the label entirely in the Ir-H positions. The second mechanism (eq 7) seems to be the correct one. When d_2-**9**, prepared from **1c** and D_2 at -78 °C, is placed under 1 atm of H_2 and allowed to warm to room temperature, most of the deuterium is lost from **9** on the time scale of several tens of seconds to give largely d_0-**9**. d_0-**9** only rearranges to d_0-**10** on the time scale of several tens of minutes. This is most



(5)

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(4) Bennett, M. A.; Crisp, G. T. *Organometallics* **1986**, *5*, 1800.

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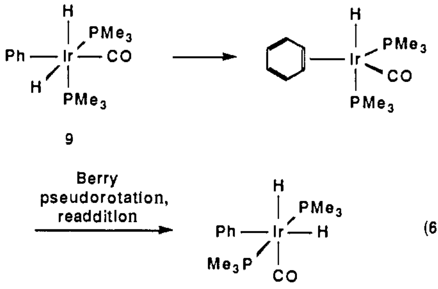
Table II. NMR Data[a] Characterizing the Direction of H_2 Addition

	^1H NMR	^{13}C NMR[b]	^{31}P NMR
$IrCl(CO)(PMe_3)_2$ (**1a**)	−18.9, dt (4.9[e], 20.5[d]), IrH, −7.8, dt (4.9[c], 14.7[d]), IrH, 1.4, t (3.65[e]), PMe		
$IrMe(CO)(PMe_3)_2$ (**1b**)	−10.05, dd (17, 130)[f], IrH, 0.21, tt (1.8[g], 19.7, t (16.6), PMe (12[h]), Me, 1.14, 7.7[j]), PMe	−41.6, s, Ir-Me	
$IrPh(CO)(PMe_3)_2$ (**1c**)	−9.78, dd (16, 130)[f], IrH, 1.13, d (8.3[j]), PMe, 7.08, *c*, 7.9, t, 8.05, d, Ph		−60.1
(thermodynamic isomer) **10**	−12.2, dt (5.3[c], 17.2[d]), IrH, −9.2, dt (5.3[c], 21.2[d]), IrH, 1.24, t (3.8[e]), PMe, 7.48 and 8.04, c, Ar		−49.5
$IrMe(CO)(PPh_3)_2$	−9.35, dd (17, 128.6)[f], IrH, 0.26, t (10.7[h]), IrMe, 7.2–8.0, c, Ar		

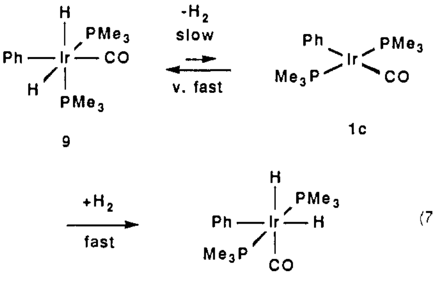
[a] In C_6D_6 and at 25 °C unless stated. [b] Gated ^1H decoupled. [c] $^2J(H,H)$. [d] $^2J(P,H\ cis)$. [e] $J_{apparent}$ for the virtually coupled triplet observed. [f] $J_{apparent}$ for the AA′XX′ pattern observed. [g] $^3J(H,H\ cis)$. [h] $^3J(P,H\ cis)$. [j] $^2J(P,H)$.

readily explained by a slow loss of H_2 from **9** to give the starting complex **1c**. This has the choice of adding H_2 in one of two ways, to give **9** or **10**. Since we know that initially essentially only **9** is formed (>98%), we can say that **1c** normally goes back to **9**, accounting for the rapid formation of d_0-**9**. Occasionally, however,



(6)

1c must add H_2 to give the parallel isomer **10**, which, being more thermodynamically stable, accumulates until it is essentially the only species (>98%) present. A similar mechanism has been proposed by Eisenberg et al.[1] for their related isomerization reactions.

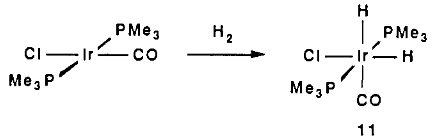


(7)

In confirmation of this picture, we found that when the isomerization was studied by ^{31}P NMR spectroscopy, a small (~2% intensity) peak was observed at −24.4 ppm during the reaction. This position corresponds to the resonance position expected for **1c**. When the isomerization was complete, no **1c** was detected.

The next question that arises is whether formation of the perpendicular isomer is unique to the PMe_3 form of Vaska's complex. An argument could be made that PMe_3, being sterically less demanding than PPh_3, can more easily become cis and so $[IrX(CO)(PMe_3)_2]$ can more easily form the parallel isomer. To test this idea, we studied $MeIr(CO)(PPh_3)_2$. Atwood et al.[6] had previously found that H_2 addition to this complex leads to loss of methane and formation of $IrH_3(CO)(PPh_3)_2$, and they naturally postulated $IrMeH_2(CO)(PPh_3)_2$ as the most reasonable intermediate but did not determine its stereochemistry. This we have now done by passing H_2 into a solution of $IrMe(CO)(PPh_3)_2$ at −82 °C. The expected dihydride intermediate is stable at this temperature and we find that the perpendicular isomer, analogous to **8**, is formed. This assignment follows from the ^1H NMR spectrum. For example, the Ir-H groups resonate in the familiar AA′XX′ pattern coupled with the two cis phosphorus nuclei ($J(P,H\ trans)$ = 129 Hz). The $Ir-CH_3$ group resonates at δ 0.25 as a triplet of triplets ($^3J(P,H\ cis)$ = 10.7 Hz, $^3J(H,H')$ = 2 Hz). On warming to 0 °C, loss of methane begins to occur and the resulting $IrH(CO)(PPh_3)_2$ is trapped by the excess H_2 present to give the known[6] *fac*-$[IrH_3(PPh_3)_2(CO)]$, the resonances for which grow in above 0 °C. With use of D_2 it has been determined that the perpendicular adduct is formed from $[IrH(CO)(PPh_3)_2]$.[7b]

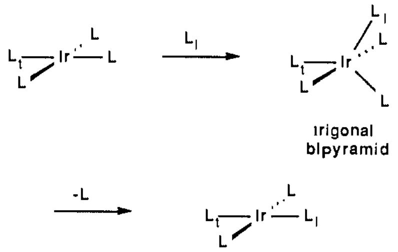
These results suggest that stereoelectronic and not steric effects are important in determining the direction of H_2 addition. We have seen that the nature of the X group in $[IrX(CO)L_2]$ is significant, and so we looked at H_2 addition to $IrCl(CO)(PMe_3)_2$, which should give the parallel adduct as the PPh_3 analogue is known to do. This adduct is indeed formed as shown in eq 8. The product **11** is a stable, isolable white solid and shows no tendency to isomerize to the perpendicular isomer in solution, although it does decompose slowly in solution even under N_2 over several weeks.



(8)

The stereochemistry shown follows from the ^1H NMR spectrum. The Ir-H resonances at δ −7.8 (trans to CO) and δ −18.9 (trans to Cl) show mutual coupling ($^2J(H,H')$ = 4.9 Hz) as well as coupling to two cis phosphorus nuclei ($^2J(P,H\ cis)$ = 20.5 and 14.7 Hz, respectively). The PMe resonance at δ 1.4 shows a virtual coupling pattern (J_{app} = 3.65 Hz) appropriate for a trans arrangement of these ligands. These spectral data are very close to those reported for the PMe_2Ph analogue.[5d]

The Origin of the Directing Effect. The results we have obtained are summarized in Table I. They clearly rule out the proposal that H_2 should always add parallel to any Ir–CO bond present. We also considered another model, based on an unpublished suggestion by Wolczanski,[8a] and also briefly considered by Eisenberg et al.[1] and illustrated in eq 9 and 10. Consider a d^8 species $M(L_t)L_3$ where L_t has a high trans effect. The argument used to explain preferential substitution of L by an incoming ligand L_i at a position trans to L_t is that L_t prefers to occupy an equatorial site in the 5-coordinate transition state (or intermediate) shown. The extension to the case of H_2 addition is shown in eq 10.



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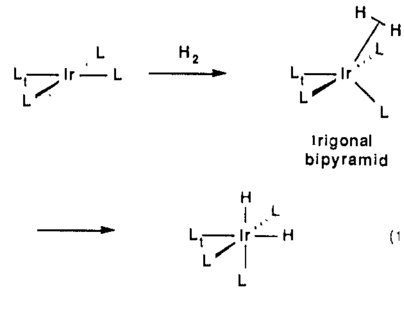
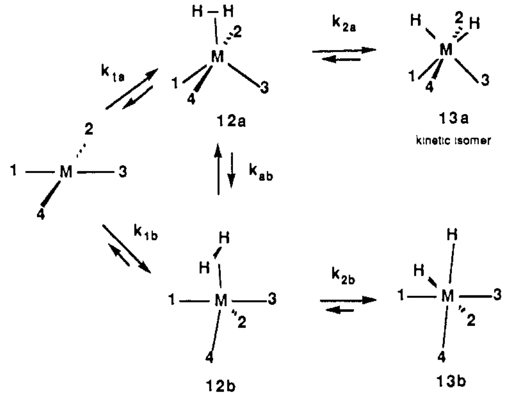


(10)

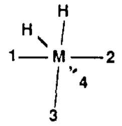
Our results apparently exclude this explanation because CO, Me, and Ph are all high trans effect ligands. [MeIr(CO)L_2] and [PhIr(CO)L_2] should therefore show a very strong tendency to give the parallel adducts, but this is not observed.[8b]

We previously suggested that the direction of addition is determined by the relative stability of two putative 5-coordinate species of types **12a** and **12b**. Only if they are transition states is this necessarily true. Now that we know that H_2 complexes are common, it is probably more reasonable to assume that **12a** and **12b** are true intermediates instead of transition states (see eq 11). We have seen that H/D exchange with free D_2 is faster than the rearrangement of the kinetic (**13a**) to the thermodynamic isomer (**13b**) in the case of $H_2IrPh(CO)(PMe_3)_2$, and so the rearrangement probably goes through the square-planar starting material. This implies that k_{ab} is slow relative to k_1. We do not know if the kinetic ratio of **13a**/**13b** is mainly decided by k_{1a}/k_{1b} or k_{2a}/k_{2b}, although the latter choice seems most reasonable. Of course, by the Hammond postulate, the relative stabilities of unstable intermediates, such as **12a** and **12b** will affect both k_{1a}/k_{1b} and k_{2a}/k_{2b}, and so our original suggestion may still have some validity.



(11)

Isomers such as **13c** are never observed in these reactions. **13c** is accessible from **12** by a pseudorotation/oxidation addition sequence if the H_2 ligand is allowed to become axial. If intermediates such as **12** do exist, we are entitled to ask why **13c** is not seen. As we saw above in k_{ab} and will meet again later, pseudorotation in 5-coordinate adducts is often relatively slow so our observations are not unexpected.



13c

Only if **12a** and **12b** could be directly observed could we verify this picture and try to find out which of the rate constant ratios in eq 11 are important in determining the outcome. In the absence of these data, we can only fall back on a plausible analogy. As described below, we have tried to make 5-coordinate adducts with alkenes and ligands such as PMe_3 to see whether these have the same stereochemistry as we observed for the H_2 adducts. Of course, these ligands differ substantially in steric and electronic character from H_2, but we were still interested to see if any general trends emerge. To anticipate our results, we find that strong π-acceptors (e.g., TCNE) tend to prefer perpendicular addition, and strong σ-donors, such as PMe_3, tend to prefer parallel addition; as we have seen, a ligand that is both a π-acceptor and a σ-donor, such as H_2, can add in either direction according to the nature of the X ligand. We rely on published theoretical studies[9] to identify the important interactions present and this has led to a picture that seems to account for the data accumulated to date.

Extended Huckel (EH) studies have shown that there are three important interactions in H_2 addition to d^8 ML_4 species.[9] The first is a 4e repulsive interaction between the filled d_{z^2} orbital and the filled $H_2(\sigma)$; this opposes the oxidative addition. As a pair of ligands L′ bend back to reach the transition state, this repulsive interaction is reduced if L′ is a good π-acceptor ligand because the metal d_{z^2} orbital is stabilized. This is the factor that favors addition when L′ = CO and, taken in isolation, it predicts that parallel adducts should always be formed in an addition to Vaska's complex. Experimentally, this is not always the case and so we must look at the other interactions found in the EH studies.

The second is a $M(d_\pi)$ to $H_2(\sigma^*)$ back-donation that cleaves the H–H bond and so encourages addition. The filled metal d orbital involved (largely d_{yz} if we define the principal axis of the TBP intermediate as x and the direction of approach of the H_2 as z) also interacts with the L′ ligands but via their σ rather than their π orbitals. Strong σ-bonding ligands, such as tertiary phosphines, probably destabilize the filled d_{yz} orbital very effectively, and so this encourages M to $H_2(\sigma^*)$ back-bonding and therefore favors perpendicular oxidative addition. We refer to this effect as homo-directed oxidative addition because it is the metal homo that decides the outcome. This cannot be studied effectively by EH methods because the calculated energy of the $H_2(\sigma^*)$ orbital is much higher than the observed value, and so the back-bonding would be underestimated.

The third reaction that has been identified is donation from the filled $H_2(\sigma)$ into the empty $M(p_z)$ orbital in the transition state. The presence of π-donors, such as Cl^-, in the square plane destabilizes the $M(p_z)$ lumo. By bending of the π-donor out of the plane, this destabilizing interaction is reduced. Therefore when Cl and CO bend out of the plane, we can refer to lumo-directed oxidative addition.

To summarize the argument, it is the nature of the equatorial ligands, 1 and 3 in **12a** and 2 and 4 in **12b**, that controls the direction of addition. We believe that three effects are important.

(i) Equatorial ligands that are good π-acceptors (CN and CO) stabilize the filled d_{z^2} orbital and reduce the 4e repulsive interaction between it and $H_2(\sigma)$ and so encourage H_2 addition.[9] An alternative way of thinking of this is to argue that π-acceptor ligands prefer to be in the equatorial plane of a TBP d^8 species.

(ii) Equatorial ligands that are good σ-donors make the metal more π-basic by raising the energy of the d_{yz} orbital, which back-bonds more effectively into the $H_2(\sigma^*)$ and cleaves the H–H bond more efficiently.

(iii) When equatorial ligands are good π-donors, the $M(p_z)$ orbital is stabilized and the oxidative addition encouraged.

When H and CO are mutually trans, factor (ii) decides the result and the homo-directed perpendicular adduct is observed. When Cl and CO are mutually trans, then factors (i) and (iii) predominate and the lumo-directed parallel adduct is observed.

This model resembles our earlier one in emphasizing factors that lead to changes in the relative stabilities of **12a** with respect to **12b**, but it also goes on to consider the relative π-donor character of the metal in the two different transition states, however, and here we are looking at an interaction that alters the ratio of k_{1a} and k_{1b}. If this analysis is right, it is the second kinetic factor that is chiefly responsible for causing the changeover from parallel to perpendicular H_2 adduct formation on going from X = Cl to X = Me or Ph in [IrX(CO)L_2)].

Alkene and Related Adducts of 1. As discussed above, we have also looked at some alkene adducts of **1** to see if the direction of alkene addition is the same as that of H_2 addition.

Data from the literature is not uniformly encouraging. For example, although [IrBr(CO)$(PPh_3)_2$] gives a parallel H_2 adduct, it gives a perpendicular TCNE adduct.[10] On the other hand,

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(8) (a) Wolczanski, P. J., personal communication, 1986. (b) Eisenberg[8c] points out that CO and Me or Ph are high trans effect ligands for quite different reasons, CO is a strong π-acceptor, and Me or Ph is a strong σ-donor. Me and CO might therefore have a strong tendency to remain mutually trans by the antisymbiotic[8d] effect. (c) Eisenberg, R., personal communication, 1988. (d) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.

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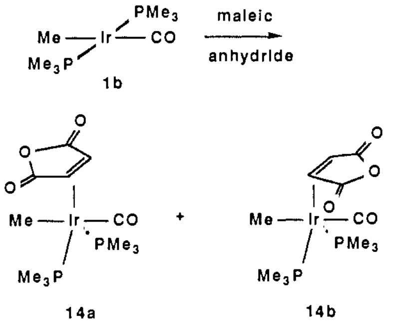
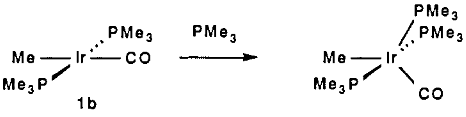
[IrH(CO)$(PPh_3)_3$] gives a perpendicular H_2 adduct (as would be predicted from the discussion in the last section) and gives a perpendicular fumaronitrile adduct.[11]

We looked at [IrMe(CO)$(PMe_3)_2$] (**1b**) as having minimal steric effects that might otherwise obscure the conclusions. The complex reacts rapidly with C_2H_4 to give an adduct. Unfortunately it was not possible to be completely certain of the stereochemistry of this adduct. The incompletely virtually coupled PMe resonance at δ 1.21 (J_{app} = 4 Hz) is the best evidence that the perpendicular isomer is formed. A definitive characterization was possible only for the maleic anhydride (MA) adduct, which is unambiguously perpendicular. This is shown most clearly by the formation of two isomers **14a** and **14b**, in both of which virtual coupling of the PMe_3 groups is lost. The parallel adduct would be expected to give only one isomer in which virtual coupling is retained. It is notable that **14a** and **14b** do not exchange on the NMR time scale at 25 °C. This suggests that the adduct may have considerable metalacyclopropane character, and so the alkene does not undergo rapid rotation. This would in turn suggest that the important orienting factor in this case is the metal d_{yz} to alkene (C=C)π^* back-donation (this is the second of the two factors we identify as being important in H_2 addition). The fact that [IrBr(CO)$(PPh_3)_2$] gives a perpendicular TCNE adduct (its H_2 adduct is parallel) can be rationalized on the same basis. The direction of addition for the strongly π-accepting TCNE is dominated by the metal to C=C π^* component of the bonding, not the stabilization of d_{z^2} and p_z. For H_2 addition, the latter seems to be at least as important as the former in deciding the direction of H_2 addition.



(12)

We also added PMe_3 to **1b** and found that the parallel adduct[12] is formed, in contrast to the perpendicular adduct formed with H_2. This difference can be explained by noting that PMe_3 is a poor π-acceptor. For such a ligand, the 4e repulsive interaction mentioned above will dominate the situation, and the parallel adduct will tend to be formed by lumo control.



(13)

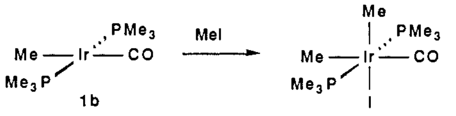
The stereochemistry of the adduct follows from the spectral data for the isolable, white IrMe(CO)$(PMe_3)_3$. The complex contains two equivalent and virtually coupled PMe_3 groups (δ 1.63, J_{app} = 3.8 Hz) as well as a single isolated PMe_3 (δ 1.53, d, ^2J(P,H) = 9.8 Hz). The Ir-Me group shows a doublet of triplets (^3J(P,H) axial = 3.3 Hz, ^3J(P,H) equatorial = 6.6 Hz) as expected for coupling to one equatorial and two axial PMe_3 phosphorus nuclei.

The direction of addition therefore depends on the electronic character of the addendum. Neither TCNE nor PMe_3 are good models for H_2. The direction of addition for TCNE is dominated by metal to ligand back-bonding and is therefore homo-directed and for PMe_3 by minimizing the 4e repulsion effects (lumo-directed). H_2 itself lies somewhere between these two extremes and so shows sensitivity to such relatively small effects as changing X from halide to Me, Ph, or H.

Although only two cases have been studied, CO follows H_2 in the direction of H_2 addition, a parallel adduct being known for IrCl(CO)$(PPh_3)_2$[13] and IrCl(CO)$(PMe_3)_2$.[2b]

Other Adducts of 1b. The addition of excess anhydrous HCl to **1b** in C_6H_6 gives the known[14] *cis,trans*-[$IrHCl_2$(CO)$(PMe_3)_2$]. Presumably, **1b** protonates to give the reactive 16e cation [IrHMe(CO)$(PMe_3)_2$]$^+$, which rapidly loses CH_4. Addition of Cl^- and HCl gives the final product.

The addition of methyl iodide to a solution of **1b** in C_6D_6 gave the colorless *cis,trans*-[$IrIMe_2$(CO)$(PMe_3)_2$], the ^1H NMR spectrum of which indicated the formation of the single isomer shown. The PMe_3 groups are virtually coupled (δ 1.27, J_{app} = 3.8 Hz). The Ir-Me groups are inequivalent (δ 0.51 and 0.49) and coupled to two phosphorus nuclei. The mechanism of this reaction may be an S_N2 attack as is known[15] for the chloro analogue **1a**, and so not relevant to the problem of concerted additions. We expect MeI addition to **1b** to be trans, and indeed, only one isomer of the CD_3I adduct is observed, although we were not able to determine its stereochemistry unambiguously.



(14)

1b failed to react with benzene on reflux for 3 h. Similarly, the phenyl analogue **2c** failed to react with C_6D_6 under the same conditions.

Conclusion

We have shown that the current models are inadequate to explain the stereochemistry of the H_2 adducts formed by d^8 square-planar complexes. We propose a new model that seems to cover all the examples known to date. The model also rationalizes the effect of changing the addendum from H_2 to such species as FMN and PMe_3. The direction of addition of a strongly π-acceptor addendum will be dominated by factor (ii) discussed above, and perpendicular adducts will be formed even for IrCl(CO)L_2. For a strongly σ-donating addendum such as PMe_3, factors (i) and (iii) will dominate and parallel adducts will be formed even for IrMe(CO)L_2. This work suggests how rational syntheses of various stereoisomers of d^6 ML_6 complexes can be planned. Further endeavors along these lines should provide a searching test of the proposed directivity effects.

Experimental Section

Preparative work was performed under purified Ar in Schlenk apparatus.

Methyl(carbonyl)bis(trimethylphosphine)iridium(I). To [IrCl(CO)$(PMe_3)_2$] (**1a**, 384 mg, 0.94 mmol) in C_6H_6 (20 mL) was added MeLi (1.28 mL of a 1.1 M Et_2O solution, 1.41 mmol) at room temperature. The mixture was stirred for 45 min and filtered through Celite, and the resulting yellow solution transferred to an oven-dried sublimation apparatus. The solvents were carefully removed under reduced pressure and the residue sublimed at 50 °C (10^{-3} Torr) for 3–4 h. A submersible pump circulated ice water through the cold finger of the sublimator (using water at 25 °C reduces the yield). The product was collected as very air sensitive, bright yellow crystals in 71% yield (0.26 mg). Anal. Calcd for $C_8H_{21}P_2OIr$: C, 24.81; H, 5.47. Found: C, 24.95; H, 5.39. ^1H NMR (C_6D_6): δ 0.43, t (^3J(P,H) cis) = 9.8 Hz), IrMe; 1.29, t (^2J(P,H) = 3.3 Hz), PMe. ^{13}C NMR (C_6D_6): δ 1.8, s, IrMe; 16.4, t (^2J(P,C) = 17.4 Hz), PMe; 187.2, t (^2J(P,C) = 10 Hz), CO. ^{31}P NMR (C_6D_6, relative to external 85% H_3PO_4): −23.65 ppm.

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Phenyl(carbonyl)bis(trimethylphosphine)iridium(I). To [IrCl(CO)(PMe_3)$_2$] (**1a**, 629 mg, 1.54 mmol) in C_6H_6 (30 mL) was added PhLi (0.93 mL of a 2 M solution in 70:30 v/v cyclohexane/ether, 1.85 mmol), and the mixture was stirred for 40 min at 25 °C. The resulting solution was filtered through Celite and concentrated under reduced pressure to ca. 3 mL. Heptane (8 mL) was added to precipitate the product as a very air sensitive solid in 69% yield (478 mg). Anal. Calcd for $C_{13}H_{23}P_2OIr$: C, 34.74; H, 5.16. Found: C, 34.55; H, 5.13. ^1H NMR (C_6D_6): δ 1.10, t (^2J(P,H) = 3.4 Hz), PMe; 7.01, tt, 7.28, t, 7.46, dd, para, meta, and ortho H. ^{31}P NMR (C_6D_6): −24.4 ppm.

Dihydrogen Adducts of Vaska's Complex 1. Through a solution of **1** (0.05 mmol) in C_6D_6 (0.5 mL) at 25 °C in an NMR tube was bubbled H_2 (1 atm) for 5 min. The solution turned from yellow to colorless and the ^1H NMR spectrum was immediately recorded. The data reported in Table **II** show the spectral characteristics of the adducts which characterize the direction of addition in each case. The isomerization of **9** to **10** was most conveniently followed by ^{31}P NMR spectroscopy (see Table II). During the isomerization a peak was observed for IrPh(CO)(PMe_3)$_2$ at −24.4 ppm. Only one of these adducts, [H_2ClIr(CO)(PMe_3)$_2$] was stable enough to analyze. Anal. Calcd for $C_7H_{20}P_2OClIr$: C, 20.50; H, 4.92. Found: C, 20.51; H, 4.84.

Other Adducts of 1b. Anhydrous HCl was bubbled into [IrMe(CO)(PMe_3)$_2$] (**1b**, 13.9 mg, 0.036 mmol) in C_6D_6 (0.5 mL) in an NMR tube, and the ^1H NMR spectrum was recorded. Quantitative conversion to the known *cis,trans*-[IrHCl_2(CO)(PMe_3)$_2$] was indicated by the spectral data: −17.08, t (J = 12.8 Hz), Ir-H; 1.28, t (J = 4.1 Hz), PMe.

To sample of **1b** (11 mg, 0.028 mmol) was added MeI (1.8 μL, 0.028 mmol). The ^1H NMR spectrum of the resulting colorless solution showed quantitative conversion to 1,2,6,4,3,5-[IrMe_2I(CO)(PMe_3)$_2$]: δ 0.49 and 0.51, t (^3J(P,H) = 5.8 and 9 Hz), IrMe; 1.27, t (virtual coupling J_{app} = 3.8 Hz), PMe.

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Decamethylrhenocene, (η^5-C_5Me_5)$_2$Re

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Contribution from the School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K., the Department of Chemistry, University of York, York Y01 5DD, U.K., the School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K., the Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K., and the Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, U.K. *Received August 13, 1987*

Abstract: The synthesis of Cp*$_2$ReH (Cp* = η^5-C_5Me_5) from Re vapor and C_5Me_5H and its photochemical conversion into Cp*$_2$Re are described. The X-ray crystal structure of the latter has been determined and shows the molecule to possess the parallel ring, eclipsed, sandwich structure (space group $P2_1/m$, a = 8.620 (3), b = 14.593 (5), c = 7.923 (3) Å, Z = 2, refinement on 1871 reflections, R_w = 0.037). The solid-state magnetic moment reveals Curie–Weiss behavior consistent with a $^2A_1$ (or $A_{1/2}$) ground state. Visible absorption and laser-induced fluorescence spectra in Ar and N_2 matrices showed a strong LMCT band with excellently resolved vibrational structure. The same transition is observed at room temperature in solution. Magnetic circular dichroism (MCD) spectra in Ar matrices show an intense signal with an inverse temperature dependence of intensity (C term). The value of $g_{\parallel}$ is determined from the magnetization curve of the MCD spectrum as 4.87 (19). Measurement of the ESR spectrum of Cp*$_2$Re in frozen toluene at 4 K showed that the molecule also has an $E_{5/2}$ ground state under these conditions with $g_{\parallel}$ = 5.081 (3), A_{Re} = 1585 (3) MHz. The gas-phase photoelectron spectrum (He I and He II) proved inconsistent with an $E_{5/2}$ state for the neutral molecule and is best described by an equilibrium between $A_{1/2}$ and $E_{5/2}$ states. The value of the solution magnetic moment at room temperature (μ_{eff} = 1.95 (10) μ_B) also suggests an equilibrium between electronic states.

There is overwhelming evidence that the electronic structure of the metallocenes and other parallel sandwich complexes is well described by the ligand field model.[2-5] According to the LF model the d orbitals are split into three sets: in order of decreasing binding energy e_2 (xy, $x^2 - y^2$), a_1 (z^2), and e_1 (xz,yz). (We use symbols indicating D_5 or D_6 symmetry, since various rotamers may be present.) When the complex has a d^5 configuration, the choice of electronic ground state is very sensitive to the particular combination of metal and ligand. Of the three possible configurations (Figure 1), the $^2A_1$ state is adopted by all the bis(arene) metal complexes,[6] while Cp_2Fe^+, Cp*$_2Fe^+$, and Cp*$_2$Mn adopt $^2E_2$ states (Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5).[2-4,7,8] In contrast, Cp_2Mn and (η^5-C_5H_4R)$_2$Mn either may be switched between $^2E_2$ and $^6A_1$ states by a change of host material or exhibit an equilibrium between them.[3,5,9] The $^2E_2$ state is subject to Jahn–Teller distortion which has been observed as both dynamic and static effects on the ESR spectra of manganocenes.[5,9] A significant distortion from D_{5d} symmetry has been established for Cp*$_2$Mn in the crystal.[10]

In contrast to the first-row metallocenes, the d^5 configuration appeared until now to be highly unstable for third-row metallocenes. Thus the only metallocene characterized was rhenocene, Cp_2Re, formed by photolysis of Cp_2ReH in CO or N_2 matrices at ca. 20 K.[11] For a third-row metal, the $^2E_2$ state is subject to

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