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The Antisymbiotic Effect in some Iridium(III) Hydrides with N-, O-, and S-Donor Ligands

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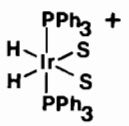
Some complexes of the type cis, cis, trans-*[$IrH_2S_2L_2$]BF_4 (1, L = PPh_3; S = NH_3, $PhNO_2$, ½ thianthren, and other ligands) are described and discussed in terms of the antisymbiotic effect.*

Introduction

The tendency of soft ligands to congregate in metal complexes was termed symbiosis by Jorgensen [1] in 1964. Soft ligands [2, 3] generally render a central metal more polarisable and hence more ready to bind other soft ligands. Chatt and Heaton [4] pointed out that a soft ligand could encourage the binding of hard bases in the *trans* position. This was later termed the antisymbiotic effect by Pearson [5]. The antisymbiotic effect has been used to rationalize a variety of effects such as the mode of binding [6] of SCN^- and the stability of certain platinum metal complexes of hard-donor ligands [7]. It is argued [4, 5] that two soft ligands in *trans* positions will have a mutually destabilizing effect, so that in the *trans*-arrangement L^1–M–L^2 a stabler complex will result when L^1 is soft (high *trans* effect) and L^2 is hard than when both L^1 and L^2 are soft since in the latter case both will compete for the same metal d-electrons.

These ideas have proved useful for discussing which of several possible isomers of a compound will be thermodynamically the most stable.

The complexes *cis, cis, trans*-[$IrH_2S_2L_2$]BF_4 [8] *1* (S = H_2O, MeOH, and related ligands; L = PPh_3) seem to show the effect well. The highest *trans*-effect ligands, H are opposite the lowest *trans*-effect ligands, S. The ligands having intermediate *trans*-effect must then be mutually *trans*, as also expected on steric grounds. In addition, many hard ligands are bound (S = H_2O, MeOH, Me_2CO) that are not often found in organometallic complexes. We wondered whether the antisymbiotic effect of the hydride ligands was responsible for the ease of binding of these ligands. If so, other organic compounds, not normally found as ligands in organometallic complexes, might also bind. We were therefore interested to discover how wide a range of compounds, both hard and soft, could be bound. Among the hard ligands we studied were NH_3 and two esters, and among the soft ligands, a chelating thioether as well as some halocarbons.



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Synthesis of the New Complexes

The usual way of preparing complexes of type *1*, hydrogenation of [Ir(cod)L_2]BF_4 (cod = 1,5-cyclooctadiene) in the presence of S, fails in the case S = NH_3, because reaction [9] competes with the desired route, eqn. 2.

$$[Ir(cod)L_2]^+ + NH_3 + 5H_2 \rightarrow IrH_5L_2 + NH_4^+ + \text{cyclooctane} \quad (1)$$

$$[Ir(cod)L_2]^+ + 2\,NH_3 + 3\,H_2 \rightarrow IrH_2(NH_3)_2L_2^+ + \text{cyclooctane} \quad (2)$$

This was so whether the reaction was carried out in aqueous NH_3 or if H_2 was first passed through saturated aqueous NH_3 and then over solid [Ir(cod)L_2]BF_4.

The desired complex can be prepared by displacing H_2O or Me_2CO from *1* (S = H_2O or Me_2CO). If N_2 is passed through satd. aq. NH_3 and then over the solid *1* for six hours, a 90% yield of *1* (S = NH_3)

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is obtained after recrystallization from CH_2Cl_2/Et_2O.

The ^1H NMR spectrum showed an IrH resonance at −21.5 δ (triplet, J(PH *cis*) = 17 Hz.) and an NH resonance at 1.8 δ (broad). IR spectroscopy (CH_2Cl_2, 25 °C) showed a broad ν(IrH) at 2174 cm^{-1} (w) as is found for all the complexes of type *1* [8], and a ν(NH) band at 3366 cm^{-1} (w). Attempts to deprotonate the coordinated NH_3 failed, nor was it possible to obtain analogous complexes with NEt_3 or diazabicyclooctane. The NH_3 was rather weakly bound since it was displaced by MeCN to give *1* (S = MeCN).

Although NH_3 is a common ligand in coordination chemistry, ammine hydrides are rare. $[RhH(NH_3)_5]^{2+}$ and its substitution products constitute one of the few extensive series known [10].

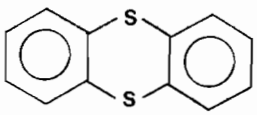
Other hard ligands not usually known in organometallic chemistry were also observed to complex. For example $PhNO_2$ displaces Me_2CO from *1* to give a complex showing a new Ir–H triplet resonance in the ^1H NMR at −22.9 δ. This species was isolated with Et_2O; analytical data indicated that one $PhNO_2$ was bound. The IR of the complex, (νNO_2 = 1483 and 1436 cm^{-1}) suggests a chelating mode of binding, as is adopted by the isoelectronic rhodium carboxylate complexes [11]. Other nitro compounds behaved similarly but the products were not isolated, being less stable, *e.g.*, *o*-nitrotoluene, *p*-nitroaniline. Nitromethane gave a mixture of products which were not investigated further.

An η^6- mode of binding is unlikely for $PhNO_2$ on the basis of the 18 electron rule: a complex containing two PPh_3 groups and hydride ligands cannot also contain an η^6-arene group. We have made arene complexes from *1*, but these have the formulation $[(\eta^6\text{-arene})IrL_2]BF_4$ [12].

We next studied the interaction of the ester group. One would expect this to be even more weakly ligating than NH_3 or $PhNO_2$. Previous results [13] suggested that an organic carbonyl group binds more strongly if it has a C=C group in conjugation. Presumably this arises from the lowering of the π* levels of the CO group, allowing better metal to ligand back bonding.

Two equivalents of ethyl cinnamate PhCH=CHCO$_2$Et, displaced Me_2CO from *1* to give a species in which a new IrH triplet was observed at −23.2 δ. The ligand may be bound in an η^2 fashion via the C=C unit or in an η^1 fashion via the C=O oxygen. The latter is most likely because the CH vinyl resonances are hardly shifted from the free-ligand value, as they would be if the ester were bound via the C=C group and because the IrH resonance position is consistent [8] with O- but not C=C-binding. No crystalline complex could be isolated from these preparations, but the ester could be displaced by two equivalents of MeCN, to give the known $[IrH_2(MeCN)_2L_2]BF_4$. No hydrogenation of the ester was observed; this might have been expected if it were C=C bound [8]. This binding may well account for the fact that $[Ir(cod)(PMePh_2)]PF_6$ was found not to reduce PhCH=CHCO$_2$Et under our usual catalytic conditions; other olefins, in contrast, are easily reduced even in the presence of CH_3CO_2Et [14]. Ethyl hydrocinnamate lacks the conjugation with the ester group and does not bind to *1* under analogous circumstances. No other organometallic O-bound ester complexes are apparently known.

We were also interested in the cases of soft donor groups and for this reason examined thianthrene and various halocarbons. Thianthrene, a bis-thioether, displaces Me_2CO from *1*



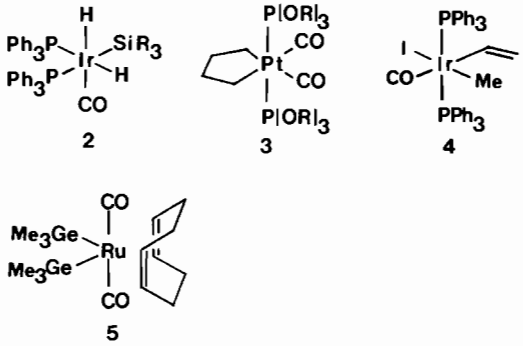
to give an isolable complex $[IrH_2(C_{12}H_8S_2)L_2]BF_4 \cdot CH_2Cl_2$ in which the thianthrene seems to be acting as a chelate. The IrH resonance in the ^1H NMR appears at −19.7 δ. An η^6-arene formulation is excluded by the 18 electron rule and because the two phenylene groups are equivalent in the ^1H NMR. This is a rare example of an organometallic thioether complex [15]. The ligand is not strongly bound as it can be displaced with MeCN to give *1* (S = MeCN).

We also examined the reaction of H_2S with *1* (S = H_2O) to try to obtain *1* (S = H_2S). A reaction occurs in the solid state on passing H_2S, but the resulting material slowly decomposes on standing if the H_2S atmosphere is removed. A ^1H NMR spectrum, obtained quickly, showed an IrH triplet at −17.06 δ. The addition of MeCN (2 equivs) led to the formation of *1* (S = MeCN). These results are consistent with the formation of *1* (S = H_2S), but we have so far been unable to get corroborative evidence from IR and microanalysis because of the instability of the complex.

As we have reported [16], halocarbons such as *o*-diiodobenzene and MeI also displace Me_2CO from *1*. In one case a crystal structure was obtained for the chelating $C_6H_4I_2$ complex. Here again, a group of ligands not known for binding to metals bind strongly to *1*, in this case *via* the halogen groups.

The fact that hard ligands S, *e.g.*, H_2O or NH_3, readily bind to *1* in a position *trans* to the soft hydrogen ligand seems to be easy to rationalize on the basis of the classical antisymbiotic effect. But these ideas do not account for the binding of the soft π-acceptor ligands thianthrene and *o*-diiodobenzene, the latter previously unknown as a ligand.

It is possible to consider the antisymbiotic effect in a different way, one that makes it consistent with our results. We can abandon the idea of antisymbiosis between soft and hard ligands, and consider instead the interaction of mutually *trans* σ and π bonds. For example, a ligand with a strong tendency to form σ-covalencies, *e.g.*, H or CH_3, may give rise to a *trans* site apt for forming π-bonds with the *trans* ligand (in this case: S). On the other hand, a ligand which forms strong π-bonds *e.g.*, CO or C_2H_4 would most readily accomodate a strongly σ-bonding *trans* ligand. Thus high *trans*-effect ligands now fall into two distinct classes with regard to the antisymbiotic effect: The σ-binding ligands H and alkyl, and the π-binding ligands, C_2H_4 and CO. On the basis of the ideas presented above, H or R would tend to prefer a site *trans* to CO or C_2H_4, rather than avoid it, as the classical view would predict. Indeed, many complexes show this arrangement of ligands, for example, *2* [17], *3* [18], *4* [19] and *5* [20], shown below:



Care must be exercised in using these ideas, because steric effects, solvent polarity, and chelation must also play a role. It is also important to be sure one is considering the thermodynamic rather than the kinetic isomer. Further work will be required to test these ideas.

If this is true, the binding of the hard ligands H_2O and NH_3 to *1* is not a result of the antisymbiotic effect. We believe the positive charge on the complex may be responsible; this will be discussed in more detail elsewhere [21]. Briefly, net positive charge on a complex ion (*i.e.* 1+ in $[Co(NH_3)_4Cl_2]Cl$) tends to be delocalized over the ligands. Hard ligands are especially effective in this respect. The positive charge, therefore, makes the metal a good σ-acid. It is striking that of the organometallic complexes which contain hard ligands [22], almost all are complex cations and many have a net charge of 2+, *e.g.*, $[(C_6H_6)Os(H_2O)_3]^{2+}$ [23] $[Pd(dpe)(thf)_2]^{2+}$ [24], $[(C_5Me_5)Rh(Me_2CO)_3]^{2+}$ [25] $[Pd(MeCN)_4]^{2+}$ [26] and $[Rh(dpe)(MeOH)_2]^{+}$ [27]. The unusual range of S ligands, soft and hard, bound by the system $[IrH_2S_2L_2]^{+}$ may therefore, be due to the unusual combination of a positive charge, which allows hard ligands to bind, and H ligands *trans* to S which encourages soft ligand binding. On these ideas, the iridium site is both a good σ-acid and a good π-base, and cannot be described simply as hard or soft.

Experimental

NMR Spectra were recorded on a Bruker HX-270 in $CDCl_3$ at 25 °C and IR spectra on a Nicolet 5000 instrument. Microanalyses were by Galbraith Laboratories Inc. Syntheses were performed under N_2, although the complexes were not air-sensitive.

Diamminedihydridobis(triphenylphosphine)iridium-(III)tetrafluoroborate

N_2 was bubbled through concd. aq. NH_3 and then into a flask containing $[IrH_2(H_2O)_2(PPh_3)_2]BF_4$ [8] (100 mg) for 6 hr. The resulting white solid was recryst. from CH_2Cl_2/Et_2O (Yield 90 mg, 90%). *Anal.* Calcd. for $C_{36}H_{48}N_2P_2F_4BIr \cdot H_2O$: C, 50.41; H, 4.70; N, 3.26. Found: C, 49.81; H, 4.56; N, 2.88%. ^1H NMR spectrum [reported as: position (δ, p.p.m.), multiplicity, (coupling const. Hz), assignment] −21.5, t (17), IrH; 1.7, s, NH_3; 7.1–7.4, c, PPh_3.

Nitrobenzenedihydridobis(triphenylphosphine)iridium(III)tetrafluoroborate

$[IrH_2(Me_2CO)_2L_2]BF_4$ (100 mg) in CH_2Cl_2 (10 ml) was treated with $PhNO_2$ (0.5 ml), and the product isolated with Et_2O, as an oil that crystallized on standing to give an orange solid. Recrystallization from CH_2Cl_2/Et_2O gave 65% of a crystalline material. *Anal.* Calcd for $C_{43}H_{37}NO_2P_2F_4BIr \cdot CH_2Cl_2$: C, 50.8; H, 3.7; N, 1.38. Found C, 50.52, H, 3.97; N, 1.56%. I.r. bands (cm^{-1}, CH_2Cl_2 solution): 1527, w*; 1483, m; 1436, s; 1349, w*, $\nu(NO_2)$. The bands marked with an asterisk seem to be those of some free $PhNO_2$. This may be a contaminant in the sample or be formed by displacement of $PhNO_2$ by adventitious H_2O. 2193, w, ν(IrH). ^1H NMR: −22.9, t(14), IrH, 7.1–74, c, PPh_3 and $PhNO_2$.

Interaction of $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ with Esters

To $[Ir_2(Me_2CO)_2(PPh_3)_2]BF_4$ (30 mg) in CD_2Cl_2 (0.5 ml) in an NMR tube was added 10 equiv. of the esters. The following results were obtained. $PhCH{=}CHCO_2Et$: The resonance due to *1* (S = H_2O) at −29.8 δ was replaced by a new band at −20.5 δ. Free Me_2CO at 2.09 δ was also observed. Attempts to isolate the product were not successful. $PhCH_2{-}CH_2CO_2Et$ did not react under similar conditions.

Thianthrenedihydridobis(triphenylphosphine)iridium-(III)tetrafluoroborate

To thianthrene (0.43 g) in CH_2Cl_2 (20 ml) was added $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ (0.15 g) and the mixture stirred for 3 h. The solvent was removed and the excess thianthrene extracted with benzene (40 ml). Recrystallization of the residue (CH_2Cl_2/Et_2O) gave colorless crystals (Yield 0.11 g 65%). *Anal.* Calc. for $C_{48}H_{40}P_2S_2BF_4IrCH_2Cl_2$: C, 53.17; H, 3.83. Found: C, 53.05; H, 3.85%. ^1H NMR: −19.7, t (20), IrH; 6.65–7.28, c, C_6H_4; 7.34–7.46, c, pH.

Reaction of $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ with H_2S

Solid $[IrH_2(Me_2CO)(PPh_3)_2]BF_4$ was exposed to H_2S (1 atm., 3 ml min^{-1} flow) in a Schlenk Tube at 25 °C for 1 hr. An unstable white solid is formed. It was quickly transferred to an NMR tube. ^1H NMR (CD_2Cl_2): −17.06, t (15), IrH: 7.3–7.5, c, Ph. Addition of MeCN (2 equiv/Ir) leads to the appearance of the characteristic IrH peak for $[IrH_2(MeCN)_2(PPh_3)_2]^+$ at −20.46, t (16).

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References

1 C. K. Jorgensen, *Inorg. Chem., 3,* 1201 (1964).
2 S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev., 12,* 265 (1958).
3 R. G. Pearson, *J. Am. Chem. Soc., 85,* 3533 (1963).
4 I. Leden and J. Chatt, *J. Chem. Soc.,* 1955, 2937. J. Chatt and B. T. Heaton, *J. Chem. Soc. (A),* 2745 (1968).
5 R. G. Pearson, *Inorg. Chem., 12,* 712 (1973).
6 A. H. Norbury, *Adv. Inorg. Radiochem., 17,* 231 (1975).
7 J. A. Davies and F. R. Hartley, *Chem. Rev., 81,* 79 (1979).
8 R. H. Crabtree, P. C. Demou, D. Eden, J. M. Mihelcic, C. Parnell, J. M. Quirk and G. E. Morris, *J. Am. Chem. Soc., 104,* 6994 (1982).
9 R. H. Crabtree, H. Felkin and G. E. Morris, *J. Organometal. Chem., 141,* 205 (1977).
10 K. Tomas, J. A. Osborn, A. R. Powell and G. Wilkinson, *J. Chem. Soc., A,* 461 (1968).
11 Z. Nagy-Magos, B. Heil and L. Marko, *Transition Metal. Chem., 1,* 215 (1976).
12 R. H. Crabtree, M. F. Mellea and J. M. Quirk, *Chem. Comm.,* 1217 (1981).
13 J W. Suggs, S. D. Cox, R. H. Crabtree and J. M. Quirk, *Tet. Lett., 22,* 303 (1981).
14 G. E. Morris, Thesis, Orsay, 1976.
15 C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem., 17,* 165 (1975).
16 R. H. Crabtree, J. W. Faller, M. F. Mellea and J. M. Quirk, *Organometallics, 1,* 1361 (1982).
17 A. J. Chalk, *Chem. Comm.,* 1207 (1969).
18 R. Burt, M. Cooke and M. Green, *J. Chem. Soc., A,* 2975 (1970).
19 J. Schwartz, D. W. Hart and J. L. Holden, *J. Am. Chem. Soc., 94,* 9269 (1972).
20 S. A. R. Knox, R. P. Phillips and F. G. A. Stone, *Chem. Comm.,* 1227 (1972).
21 R. H. Crabtree, Chap. 8 of 'Homogeneous Catalysis with Metal Phosphine Complexes', Ed. L. Pignolet, in press.
22 J. A. Davies and F. R. Hartley, *Chem. Rev., 81,* 79 (1981).
23 Y. Hung, W.-J. Kung and H. Taube, *Inorg. Chem., 20,* 157 (1981).
24 J. A. Davies, F. R. Hartley and S. G. Murray, *J. Chem. Soc., Dalton,* 2246 (1980).
25 C. White, S. J. Thompson and P. M. Maitlis, *J. Chem. Soc.,* 1654 (1977).
26 R. F. Schram and B. Wayland, *Chem. Comm.,* 898 (1968).
27 J. M. Brown, P. A. Chaloner and P. N. Nicholson, *Chem. Comm.,* 646 (1978).