Dinuclear Dihydrido Complexes of Iridium(II) of the Type $[Ir(H)(\mu\text{-}SBu^t)(CO)(PR_3)]_2$ with Single Metal–Metal Bonds

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Summary $[Ir(\mu\text{-}SBu^t)(CO)(PR_3)]_2$ (I, R = Me, Ph, NMe_2, or OMe) reacts irreversibly with molecular hydrogen to give compounds of the type $[Ir(H)(\mu\text{-}SBu^t)(CO)(PR_3)]_2$ (II); ^{31}P and ^1H n.m.r. experiments indicate the formation of metal–metal single bonds in these adducts.

THE oxidative addition of molecular hydrogen to Vaska type complexes has been extensively studied[1] but relatively few examples of dinuclear-hydrido complexes of rhodium and iridium have been reported.[2] Following our studies on the reactivity of dinuclear bridged d^8 metal complexes, we now report evidence for the irreversible† oxidative addition of H_2 to new dinuclear iridium complexes[3] of the type $[Ir(\mu\text{-}SBu^t)(CO)(PR_3)]_2$ (I, R = Me, Ph, NMe_2, or OMe) in toluene solution at 25 °C. Elemental analyses, intensities ratios in n.m.r. spectra, volumetric measurements of H_2 uptake, and molecular weight data show that these adducts are best formulated as dihydrido dinuclear species (II, R = Me, Ph, NMe_2, or OMe; H : Ir = 1 : 1).

In the i.r. spectra, the ν_{Ir-H} vibrations appear in the terminal Ir–H region, *e.g.*, (II, R = Me, Ph, or OMe) 2115(br), 2132(br), and 2128(br) cm^{-1}, respectively, in hexadecane, but lower frequencies corresponding to a bridging hydride ligand have not been detected. In their deuterium analogues, the ν_{Ir-D} vibrations appear in the region 1520—1550 cm^{-1} as expected from consideration of the isotope effect.

The proton-decoupled ^{31}P n.m.r. spectrum of (II, R = Ph) at 25 °C, in $CDCl_3$, at 36·4 MHz, shows two singlets of unequal intensities, whereas the spectrum of (I) shows only one singlet in the low-field region. [For (I), $\delta = -18{\cdot}37$ p.p.m. (relative to external H_3PO_4) and for (II), $\delta = +12{\cdot}71$,

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† The term 'irreversible' is used here in the sense used by Vaska; reductive elimination of H_2 does not take place by thermal activation under reduced pressure.

62%, and $+11{\cdot}76$ p.p.m., 38%]. This leads us to assume that each singlet of (II) is attributable to one of the possible isomers of (II); such isomers might be differentiated by the relative spatial disposition of CO and PR_3 ligands, *e.g.*, *cis–trans* isomerism, and/or by the relative disposition of the thiolato bridging ligands, *e.g.*, *syn–anti* isomerism. Thus, in each isomer of (II), the ^{31}P nuclei are equivalent. The existence of these isomers is also consistent with the occurrence of three bands in the region of CO stretching frequencies and three singlets in the ^1H n.m.r. species due to the SBu^t group. [For (II, R = Ph) ν_{CO}: 1989 (vs), 1972 (w), and 1965 (w) cm^{-1} in hexadecane and τ 9·54 (31%), 9·51 (38%), and 9·45 (31%) in CH_2Cl_2].

In the ^1H n.m.r. spectra of (II) the signals due to the phosphine ligands consist of a well defined 1:2:1 triplet showing that J_{P-P} is larger[4] than in (I) where the phosphine ligands give a doublet. *e.g.*, for (I; R = NMe_2) τ 7·19 (d, $^3J_{PH}$ 10·0 Hz); and for (II; R = NMe_2) τ 7·34 (t, $^3J_{PH}$ 10·0 Hz), in CH_2Cl_2. Thus, it is important to note that the oxidative addition of H_2 to (I) is accompanied by an increase of the $^{31}P-^{31}P$ coupling through the metal atoms.

At −40 °C, the 100 MHz ^1H n.m.r. spectra of all the dihydrido dinuclear complexes (II) exhibit two triplets with different intensities in the high-field region. [For example (II, R = Ph) τ 24·14 (38%); $^2J_{PH}$ 13·2 Hz; τ 24·99 (62%); $^2J_{PH}$ 14·3 Hz; for (II, R = OMe) τ 24·60 (15%); $^2J_{PH}$ 20·6 Hz; τ 25·45 (85%); $^2J_{PH}$ 22·1 Hz, in CH_2Cl_2]. When the temperature is raised, these two triplets coalesce into a single triplet [For (II, R = OMe) the single triplet appears above +40 °C at τ 25·3]. The same pattern is observed for spectra obtained at 250 MHz, with the expected shift of the coalescence temperature. The relative intensities of the triplets, in the low exchange limit, give the same value for the ratio of isomers as the ^{31}P n.m.r. intensity data. This ratio is dependent on the nature of R. The hydride protons of each isomer are equivalent and the multiplicity of the high field ^1H n.m.r. signals may be explained by taking P–P nuclei coupling into account. The observed triplets for the equivalent hydride protons of each isomer represent the X part of a 'deceptively simple' XAA′X′ spin system.[4] The coupling constants $^2J_{P-H}$ are characteristic of a *cis* disposition[5] of hydride and phosphine ligands in both isomers.

Thus, the reaction of H_2 with dinuclear complexes (I) leads to cleavage of the H–H bond as expected, but, unexpectedly in light of a previous observation,[2b] each hydrogen atom is bound to a different metal atom. Finally in this 'one electron' oxidative addition on each metal atom, the formally d^7 Ir^{II} atoms may be linked together by single bonds which agrees with the diamagnetic behaviour of the complexes (II) and the enhancement of the J_{P-P} coupling.

(*Received, 2nd March* 1977; *Com*; 189.)

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