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

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In a recent communication [2] we have presented evidence for the homolytic activation of molecular hydrogen by the dinuclear Iridium(I) complexes of the type $[Ir(\mu\text{-}SBu^t)(CO)(PR_3)]_2$, I (R = Me, NMe_2, Ph, OMe), in which a one electron oxidative addition process on each metal atom takes place to give symmetric dinuclear complexes of Iridium(II) having the general formula $[Ir(H)(\mu\text{-}SBu^t)(CO)(PR_3)]_2$, II. Following our investigations demonstrating the existence of metal–metal bonds in these compounds, we have studied their reactivity towards electrophilic reagents and we now report the behaviour of II (R = Me, Ph and OMe) towards H^+. The results emphasize the similarity of behaviour towards protonation of these Iridium compounds and other dinuclear complexes containing metal–metal bonds [3, 4].

Results and Discussion

The protonation of the complexes II by perchloric acid in methanol gives white crystalline products for which conductimetric measurements, elemental analyses (Table I) and intensity ratios in n.m.r. spectra are consistent with dimeric monocationic species of the type

$\{[Ir(H)(\mu\text{-}SBu^t)(CO)(PR_3)]_2(H)\}^+$, III

The Ir–H vibration in the terminal region which appears for $\{[Ir(H)(\mu\text{-}SBu^t)(CO)(P(OMe)_3)]_2(H)\}^+ ClO_4^-$ at 2142 cm^{-1} is absent for the deuterium analogue $\{[Ir(D)(\mu\text{-}SBu^t)(CO)(P(OMe)_3)]_2(H)\}^+ClO_4^-$, obtained by protonation of the deuterated complex II. This first point strongly suggests a bridging position between iridium atoms of the added proton. Nevertheless, it has not been possible to detect the Ir–H stretching frequency for such a bridging hydrogen. In the CO stretching region, the infrared spectra of the protonated species have the same pattern as the starting compounds II, and the νCO are shifted by *ca.* 80 cm^{-1} to higher frequencies.

A bridging position for the added proton is also supported by ^1H n.m.r. spectra in the high field region. The resonance signals of terminal hydrides appear in the vicinity of τ23–24 for all the complexes III studied (Table II) whereas bridging hydrides appear at higher field, *ca.* τ25–26, and the peak intensities are in the expected ratio of 2:1. This high field resonance of bridging hydride is known to be a general trend of hydrido complexes of the same metal [4]. The terminal hydride signals appear as virtual triplets as the X part of a second order XAA′X′ spin system and imply in this case the coupling between equivalent phosphorus nuclei. The bridging hydride signals appear as widely separated 1.2.1 triplets owing to an hydride which is equally coupled to two equivalent phosphorus nuclei (Figure). The preceding assignments are unambiguously confirmed by the fact that only the two virtual triplets are absent in the spectrum of the deuterated compound $\{[Ir(D)(\mu\text{-}SBu^t)(CO)(P(OMe)_3)]_2(H)\}^+ClO_4^-$.

To be more exact, it should be noted that in each case studied, *two* virtual triplets for terminal hydrides and *two* triplets for the bridging hydride are observed; the spectra may be explained by the existence of two isomers as previously mentioned in the case of the starting compounds II. In addition, the existence of such isomers is also supported by the occurrence of three singlets in the Bu^t region of the ^1H n.m.r. spectra. The ratio of isomers varies with the nature of the R group.

TABLE I. Analytical Data [% found (calcd.)] for Complexes III.

Compound	C	H	D	S	Λ_M[a] ohm^{-1} cm^2 mol^{-1}
1 $[(Ir(H)(\mu\text{-}SBu^t)(CO)(P(OMe)_3))_2(H)]^+ClO_4^-$	19.85 (19.82)	4.06 (4.06)		5.81 (6.61)	92.2
2 $[(Ir(D)(\mu\text{-}SBu^t)(CO)(P(OMe)_3))_2(H)]^+ClO_4^-$	19.84 (19.78)	3.94 (3.85)	0.40 (0.41)	5.97 (6.60)	85.1
3 $[(Ir(H)(\mu\text{-}SBu^t)(CO)(PPh_3))_2(H)]^+ClO_4^-$	44.51 (44.34)	4.38 (4.13)		5.34 (5.15)	104
4 $[(Ir(H)(\mu\text{-}SBu^t)(CO)(PMe_3))_2(H)]^+ClO_4^-$					86.6

[a] Molar conductivity in methanol at 25 °C for 10^{-3} *M* concentrations.

TABLE II. Infrared[a] and 90 MHz ^{1}H n.m.r.[b] Data for Complexes III.

Compound	ν(Ir–H)[c]	ν(Ir–D)[d]	ν(C–O)[c]	τPR$_3$	J$_{(P-H)}$	τBu^t	Hydride			
							Terminal		Bridging	
							τ	^{2}J$_{(P-H)}$	τ	^{2}J$_{(P-H)}$
1	2142(br)		2069(vs)	6.07(vt)	12.5	8.60(28%)	23.48(vt)	22.8	26.12(t)	93.4
			2057(s)			8.67(44%)	23.60(vt)	22.8	26.16(t)	95.6
						8.74(28%)				
2		1535	2069(vs)	6.07(vt)	12.5	8.60			26.13(t)	92.7
			2057(s)			8.67			26.18(t)	94.1
						8.74				
3	2177(br)		2064(vs)	3.00		9.16	23.21(vt)	15.4	25.02(t)	54.8
			2051(s)			9.33	23.25(vt)	12.2	25.04(t)	55.1
						9.39				
4	2140(br)		2047(ss)	7.77(vt)	11.0	8.56	23.79(vt)	15.4	25.09(t)	55.2
			2030(s)			8.60	24.11(vt)	17.6	25.18(t)	56.6
						8.63				

[a] Units of cm^{-1}. Abbreviations: br: broad; vs: very strong; s: strong. [b] Measured in CDCl$_3$. Units of Hz for J. Abbreviations: vt: virtual triplet; t: triplet. [c] Measured in CH$_2$Cl$_2$. [d] Measured in the solid state as CsBr pellets.

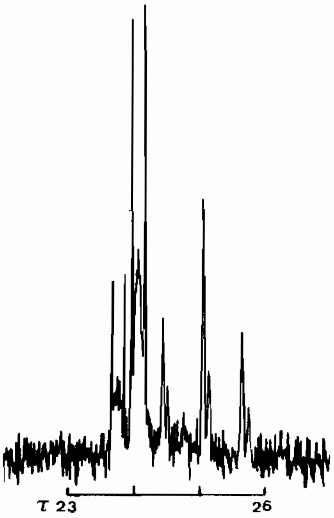

Figure.

The methyl groups of the phosphine ligands of III (R = Me, OMe) also give virtual triplets as in the case of the starting compounds II. As expected, this resonance is shifted to lower field with respect to the starting compounds and by comparison of the shape of the virtual triplets of II and III it appears that a significant decrease of the ^{31}P–^{31}P coupling is a consequence of the protonation of the iridium–iridium bond. The same decrease of the P–P coupling may be noticed in the observed pattern of terminal hydride signals.

The coupling constants ^{2}J(P–H) observed for terminal hydrides, *ca.* 12–23 Hz, are characteristic of a mutual *cis* disposition of hydride and phosphine ligands whereas those observed for bridging hydrides, *ca.* 55–95 Hz, suggest a *trans* disposition. Nevertheless, since these values are less than those characteristic of a true *trans* position in mononuclear dihydrido iridium (III) complexes (*ca.* 130–165 Hz) [5], a departure of the proton from the idealized *trans*-position with respect to the phosphine may be admitted.

It is noteworthy that no exchange between terminal and bridging hydride ligands occurs at room temperature in the case III, R = OMe; even after two weeks a solution of $\{[\mathrm{Ir(D)}(\mu\text{-SBu}^t)(\mathrm{CO})(\mathrm{P(OMe)_3})]_2(\mathrm{H})\}^+\mathrm{ClO_4^-}$ does not exhibit terminal hydride signals in the high field ^{1}H n.m.r. spectrum.

Thus, the reaction of protonation on dinuclear dihydrido Ir(II) complexes leads to symmetrical dinuclear monocationic complexes containing a two-electron three-center bent $\mathrm{Ir}\overset{\mathrm{H}}{\diagup\;\diagdown}\mathrm{Ir}$ bond as previously observed for the isoelectronic dinuclear iron(I) complexes $[\mathrm{Fe}(\mu\text{-SMe})(\mathrm{CO_2})(\mathrm{L})]_2$, L = phosphine ligands [3].

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