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Preliminary communication

Alkyl, aryl and *cis*-dihydride complexes of iridium with the tripodal phosphine $P(CH_2CH_2PPh_2)_3$ as excellent precursors of active systems for the activation of hydrocarbon C–H bonds

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Abstract

The C–H bonds of tetrahydrofuran, acetone and benzene are activated by the fragment $[(PP_3)Ir]^+$ ($PP_3 = P(CH_2CH_2PPh_2)_3$) generated either by photolytic dehydrogenation of the *cis*-dihydride $[(PP_3)IrH_2](SO_3CF_3)$ or by thermal decomposition of the *cis*-(organyl)hydrides $[(PP)_3)IrH(R)](SO_3CF_3)$ (R = Me, Ph). The latter compounds are obtained by protonation of the σ-organyl complexes $(PP_3)IrR$.

The chemistry of ML_4 systems formed by d^8 transition metals and tripodal polyphosphines such as $N(CH_2CH_2PPh_2)_3$ (np_3) or $P(CH_2CH_2CH_2PMe_2)_3$ (pp_3) is receiving considerable attention, particularly in relation to the activation of hydrocarbon C–H bonds [1,2]. However, because of the peculiar geometry of the tripodal ligands, intramolecular cleavages of C–H bonds of the phosphorus substituents has been often observed, and this presents a serious obstacle to the widespread use of d^8-ML_4 systems for the activation of hydrocarbons.

We describe here the synthesis and characterization of novel iridium complexes containing the tripodal phosphine $P(CH_2CH_2PPh_2)_3$, denoted subsequently by PP_3. In addition, we describe routes by which the highly reactive $[(PP_3)Ir]^+$ fragment can be readily generated. PP_3 is quite rigid [3] compared with the related species np_3 or the tetraphosphine pp_3, and therefore, at least in principle, the 16-electron $[(PP_3)M]$ fragment should be better for promoting intermolecular processes.

A useful starting material for the synthesis of iridium(I) derivatives of PP_3 is the cyclo-octene dimer $[Ir(C_8H_{14})_2Cl]_2$. This reacts in THF with two equivalents of PP_3 to give yellow crystals of $(PP_3)IrCl$ (**1**) (eq. 1).

$$[Ir(C_8H_{14})_2Cl]_2 + 2PP_3 \rightarrow 2(PP_3)IrCl + 4C_8H_{14} \qquad (1)$$

On protonation of **1** in THF with triflic acid, followed by addition of $NaBPh_4$ in ethanol, the Ir^{III}*cis*-(hydride)chloride complex $[(PP_3)IrH(Cl)]BPh_4$ (**2**) is obtained as

Table 1

^{1}H [a] and $^{31}P\{^{1}H\}$ [b] NMR spectral data

Compound	^{1}H		^{31}P		
	δ	J	Pattern	δ	J
1			AM_3	$\delta(A)$ 117.80 $\delta(M)$ 26.51	P_AP_M 0
2	−9.96 dxq	HP_{trans} 137.6 HP_{cis} 15.3	AM_2Q	$\delta(A)$ 102.57 $\delta(M)$ 7.46 $\delta(Q)$ 6.33	P_AP_M 4.3 P_AP_Q 4.3 P_MP_Q 10.5
3	−7.49 dxm −12.47 dxm	HP_{trans} 110.0 HP_{trans} 120.0	AM_2Q	$\delta(A)$ 120.20 $\delta(M)$ 28.01 $\delta(Q)$ 32.47	P_AP_M 4.5 P_AP_Q 4.5 P_MP_Q 7.6
4	0.70 dxq	HP_A 4.1 HP_M 4.1	AM_3	$\delta(A)$ 137.70 $\delta(M)$ 23.34	P_AP_M 0
5			AM_3	$\delta(A)$ 128.16 $\delta(M)$ 22.90	P_AP_M 0
6	−8.49 dxm	HP_{trans} 140.0	AM_2Q	$\delta(A)$ 111.55 $\delta(M)$ 13.86 $\delta(Q)$ 2.79	P_AP_M 3.7 P_AP_Q 3.7 P_MP_Q 9.8
7	−11.46 dxm	HP_{trans} 120.0	AM_2Q	$\delta(A)$ 103.46 $\delta(M)$ 9.85 $\delta(Q)$ 8.42	P_AP_M 4.0 P_AP_Q 4.0 P_MP_Q 10.0

[a] 80 MHz at room temperature. δ in ppm from external TMS. The resonances due to hydrogen atoms of the PP_3 ligand are not reported. Coupling costants in Hz. [b] 32.19 MHz at room temperature. In ppm from external H_3PO_4 85%; downfield values are assumed as positive. Coupling constants in Hz.

colorless crystals (eq. 2). The latter is quantitatively converted into the *cis*-dihydride derivative $[(PP_3)IrH_2]BPh_4$ (**3**) by prolonged reflux in THF with a large excess of $LiAlH_4$ (eq. 3).

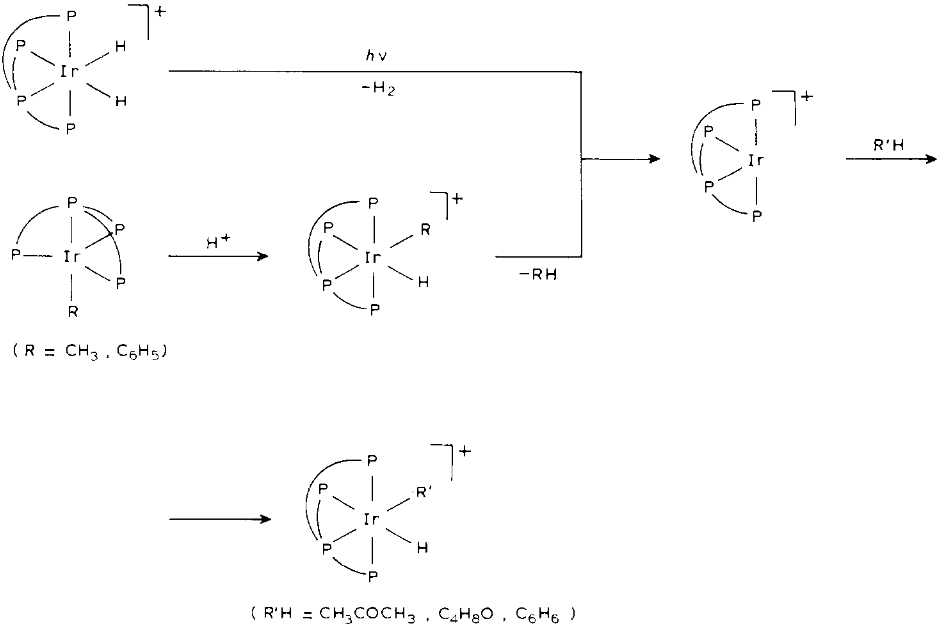
$$(PP_3)IrCl + HOSO_2CF_3 \xrightarrow{NaBPh_4} [(PP_3)IrH(Cl)]BPh_4 \qquad (2)$$

$$[(PP_3)IrH(Cl)]BPh_4 \xrightarrow{LiAlH_4} [(PP_3)IrH_2]BPh_4 \qquad (3)$$

Both compounds **2** and **3** are assigned octahedral geometries on the basis of their $^{31}P\{^{1}H\}$NMR spectra, which are those of AM_2Q spin systems (Table 1). By contrast, **1** exhibits an AM_3 pattern consistent with a trigonal-bipyramidal structure. Interestingly, in contrast to the rhodium analog $[(PP_3)RhH_2]^+$ for which we observed temperature-dependent interconversion between *cis*-dihydride ↔ η^2-dihydrogen structures [4], the *cis*-dihydride **3** retains the pseudo-octahedral geometry in solution even at very low temperatures.

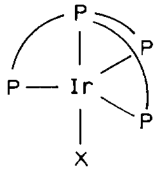
Complex **1** readily undergoes straightforward metathetical reactions with main group organometallic compounds. Thus, the alkyl and aryl derivatives $(PP_3)IrR$ (R = Me, **4**; Ph, **5**) are obtained as yellow crystalline solids by treatment of **1** in THF with the appropriate organolithium reagents.

$$(PP_3)IrCl + LiR \rightarrow (PP_3)IrR + LiCl \qquad (R = Me, Ph) \qquad (4)$$

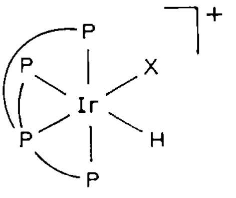


Scheme 1

The ^{31}P NMR spectra of both compounds are consistent with the presence of five-coordinate iridium in trigonal-bipyramidal arrangements. In contrast to the rhodium analogs, the σ-organyl complexes **4** and **5** do not undergo the insertion of CO into the Ir–R bonds. Such a result is not surprising for iridium [5].



(X = Cl, **1**; Me, **4**; Ph, **5**)



(X = Cl, **2**; H, **3**)

Compounds **4** and **5** are excellent precursors for formation of the highly reactive $[(PP_3)Ir]^+$ fragment by several routes, including the photolytic dehydrogenation of the *cis*-dihydride **3** and the thermal decomposition of the *cis*-(methyl)hydride $[(PP_3)IrH(CH_3)](SO_3CF_3)$ (**6**). The latter compound can be isolated as a white powder by heterogeneous reaction of **4** suspended in ethyl ether with triflic acid. Significantly, when the protonation is carried out at room temperature in tetrahydrofuran, acetone or benzene, reductive elimination of CH_4 from **6** occurs, followed by insertion of the $[(PP_3)Ir]^+$ fragment into a C–H bond of the appropriate substrate (Scheme 1) [6*].

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* Reference number with asterisk indicates a note in the list of references.

As expected, the *cis*-(phenyl)hydride $[(PP_3)IrH(Ph)](SO_3CF_3)$ (7), which can also be synthesized straightforwardly by protonation of **5**, is much more stable than its alkyl analogue towards the reductive elimination of the hydrocarbon [1].

References

1 For leading references on C–H bond activation see: R.A. Periana and R.G. Bergmann, J. Am. Chem. Soc., 108 (1986) 7332; M. Ephritikhine, Nouv. J. Chim., 10 (1986) 9; J. Halpern, Inorg. Chim. Acta, 100 (1985) 41; R.H. Crabtree, Chem. Rev., 85 (1985) 245; I.P. Rothwell, Polyhedron, 4 (1985) 77; M.L. Deem., Coord. Chem. Rev., 74 (1986) 101.

2 C. Bianchini, D. Masi, A. Meli, M. Peruzzini, M. Sabat and F. Zanobini, Organometallics, 5 (1986) 2557; M. Antberg and L. Dahlenburg, Angew. Chem. Int. Ed. Engl., 25 (1986) 260; M. Antberg and L. Dahlenburg, J. Organomet. Chem., 312 (1986) C67; C. Bianchini, A. Meli, M. Peruzzini and F. Zanobini, J. Chem. Soc., Chem. Commun., (1987) in press.

3 L. Sacconi and F. Mani in "Transition Metal Chemistry"; Marcel Dekker, New York, 1982; Vol. 8 p 179; W.H. Hohman, D.J. Kountz and D.W. Meek, Inorg. Chem., 26 (1986) 616.

4 C. Bianchini, C. Mealli, M. Peruzzini and F. Zanobini submitted for publication.

5 M.A. Lilga, Y.S. Sohn and J.A. Ibers, Organometallics, 5 (1986) 766.

6 The formation of CH_4 was detected by GLC. The reactions were monitored by ^{31}P NMR and IR spectroscopies. All of the *cis*-(organyl)hydride complexes exhibit AM_2Q spin systems and medium-intensity infrared absorptions at ca. 2100 cm^{-1}, $\nu(Ir–H)$.