

Preliminary communication

Alkyl, aryl and *cis*-dihydride complexes of iridium with the tripodal phosphine $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ as excellent precursors of active systems for the activation of hydrocarbon C–H bonds

Claudio Bianchini, Maurizio Peruzzini and Fabrizio Zanobini

*Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R.,
 Via J. Nardi 39, Firenze 50132 (Italy)*

(Received March 4th, 1987)

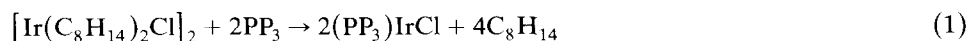
Abstract

The C–H bonds of tetrahydrofuran, acetone and benzene are activated by the fragment $[(\text{PP}_3)\text{Ir}]^+$ ($\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$) generated either by photolytic dehydrogenation of the *cis*-dihydride $[(\text{PP}_3)\text{IrH}_2](\text{SO}_3\text{CF}_3)$ or by thermal decomposition of the *cis*-(organyl)hydrides $[(\text{PP}_3)\text{IrH}(\text{R})](\text{SO}_3\text{CF}_3)$ ($\text{R} = \text{Me}, \text{Ph}$). The latter compounds are obtained by protonation of the σ -organyl complexes $(\text{PP}_3)\text{IrR}$.

The chemistry of ML_4 systems formed by d^8 transition metals and tripodal polyphosphines such as $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ (np_3) or $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3$ (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 $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$, denoted subsequently by PP_3 . In addition, we describe routes by which the highly reactive $[(\text{PP}_3)\text{Ir}]^+$ 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 $[(\text{PP}_3)\text{M}]$ 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 $[\text{Ir}(\text{C}_8\text{H}_{14})_2\text{Cl}]_2$. This reacts in THF with two equivalents of PP_3 to give yellow crystals of $(\text{PP}_3)\text{IrCl}$ (**1**) (eq. 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 $[(\text{PP}_3)\text{IrH}(\text{Cl})]\text{BPh}_4$ (**2**) is obtained as

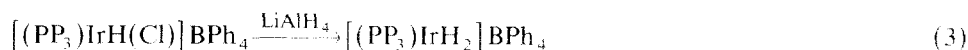
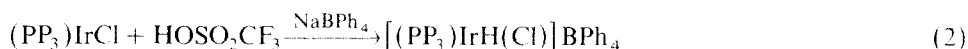
Table 1

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

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

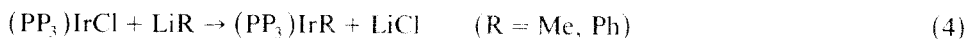
^a 80 MHz at room temperature. δ in ppm from external TMS. The resonances due to hydrogen atoms of the PP_3 ligand are not reported. Coupling constants in Hz. ^b 32.19 MHz at room temperature. In ppm from external H_3PO_4 85%; downfield values are assumed as positive. Coupling constants in Hz.

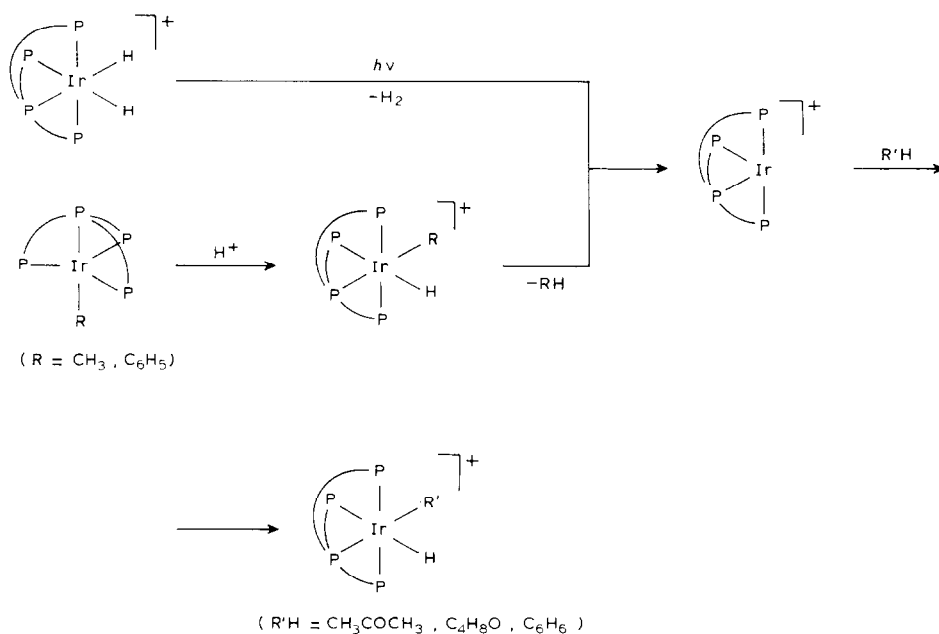
colorless crystals (eq. 2). The latter is quantitatively converted into the *cis*-dihydride derivative $[(\text{PP}_3)\text{IrH}_2]\text{BPh}_4$ (**3**) by prolonged reflux in THF with a large excess of LiAlH_4 (eq. 3).



Both compounds **2** and **3** are assigned octahedral geometries on the basis of their $^{31}\text{P}\{^1\text{H}\}$ 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 $[(\text{PP}_3)\text{RhH}_2]^+$ for which we observed temperature-dependent interconversion between *cis*-dihydride $\leftrightarrow \eta^2$ -dihydrogen structures [4], the *cis*-dihydride **3** retains the pseudo-octahedral geometry in solution even at very low temperatures.

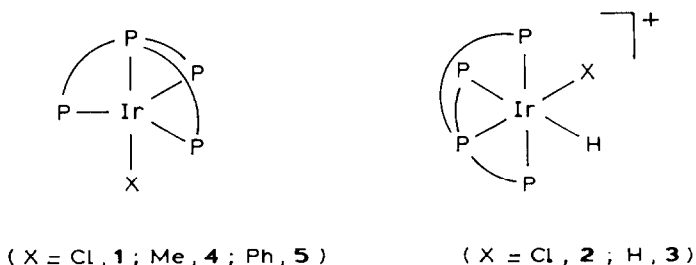
Complex **1** readily undergoes straightforward metathetical reactions with main group organometallic compounds. Thus, the alkyl and aryl derivatives $(\text{PP}_3)\text{IrR}$ ($\text{R} = \text{Me}$, **4**; Ph , **5**) are obtained as yellow crystalline solids by treatment of **1** in THF with the appropriate organolithium reagents.





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].



Compounds **4** and **5** are excellent precursors for formation of the highly reactive $[(\text{PP}_3)\text{Ir}]^+$ fragment by several routes, including the photolytic dehydrogenation of the *cis*-dihydride **3** and the thermal decomposition of the *cis*-(methyl)hydride $[(\text{PP}_3)\text{IrH}(\text{CH}_3)](\text{SO}_3\text{CF}_3)$ (**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 $[(\text{PP}_3)\text{Ir}]^+$ fragment into a C–H bond of the appropriate substrate (Scheme 1) [6*].

* 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. Zanolini, *Organometallics*, **5** (1986) 2557; M. Anthberg and L. Dahlenburg, *Angew. Chem. Int. Ed. Engl.*, **25** (1986) 260; M. Anthberg and L. Dahlenburg, *J. Organomet. Chem.*, **312** (1986) C67; C. Bianchini, A. Meli, M. Peruzzini and F. Zanolini, *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. Zanolini 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} , $\nu(Ir-H)$.