

## Synthesis of Phospha-alkene Transition Metal Complexes

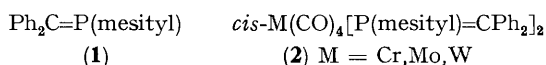
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*Summary* The first examples of co-ordination complexes containing a phospha-alkene are described; n.m.r. studies on *cis*-M(CO)<sub>4</sub>L<sub>2</sub> (M = Cr, Mo, W), *trans*-RhCl(PPh<sub>3</sub>)<sub>2</sub>L, *trans*-RhClL<sub>2</sub>(CO), Rh(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)L<sub>2</sub>, *cis*-PtX<sub>2</sub>L<sub>2</sub> (X = Cl, I, Me), and *cis*- and *trans*-PtCl<sub>2</sub>(PEt<sub>3</sub>)L, [L =

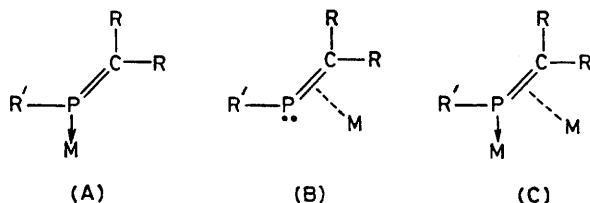
P(mesityl)=CPh<sub>2</sub>], suggest that co-ordination to the metal is *via* the phosphorus lone pair.

RECENTLY we and others<sup>1-4</sup> have developed synthetic routes to novel compounds containing carbon multiply

bonded to phosphorus, *viz.* phospho-alkenes  $R_2C=PR'$  and phospho-alkynes  $RC\equiv P$ . We now report the first examples of co-ordination complexes of the phospho-alkene  $Ph_2C=P(\text{mesityl})$  (**1**).<sup>3</sup>



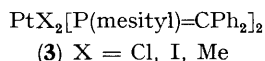
In principle, phospho-alkenes can co-ordinate to transition metals in any of the three modes (A)—(C), but so far we have found evidence only for type (A).



The red complex (**2**;  $M = Mo$ ) is obtained by displacement of norbornadiene from  $Mo(CO)_4(C_7H_8)$ ; alternatively, the series of Group 6B metal tetracarbonyl complexes (**2**) can be made from  $[M(CO)_5Br]^-$ . Treatment of  $W(CO)_5(\text{thf})$  ( $\text{thf} = \text{tetrahydrofuran}$ ) with (**1**) gives a mixture of (**2**;  $M = W$ ) and  $W(CO)_5[P(\text{mesityl})=CPh_2]$ . The latter can also be obtained in poor yield by dehydrochlorination of  $W(CO)_5[PCl(\text{mesityl})CHPh_2]$  with *dbu* (*dbu* = 1,5-diazabicyclo-[5.4.0]trans-undec-5-ene).

The i.r. spectra of (**2**) exhibit the expected four  $\nu(\text{CO})$  bands and the  $^{31}\text{P}$  n.m.r. data [ $M = Cr$ ,  $\delta_p$  237;  $M = Mo$ ,  $\delta_p$  223;  $M = W$ ,  $\delta_p$  195 p.p.m. (all to low field of  $H_3PO_4$ )] show the expected shift variations expected for simple phosphine complexes along the series.<sup>5</sup> The  $^{31}\text{P}$  n.m.r. spectrum of (**2**;  $M = W$ ) also exhibits satellite lines from coupling to  $^{183}\text{W}$  ( $I \frac{1}{2}$ , 14.3% abundant) [ $^1J(\text{WP})$  264 Hz] establishing phosphorus as the donor atom. The  $^{13}\text{C}$  n.m.r. spectrum of (**2**;  $M = Mo$ ) is very similar to that of the free phospho-alkene with additional resonances at 204.7 and 214.3 p.p.m. for the pairs of CO-ligands, again favouring co-ordination of type (A) rather than (B).

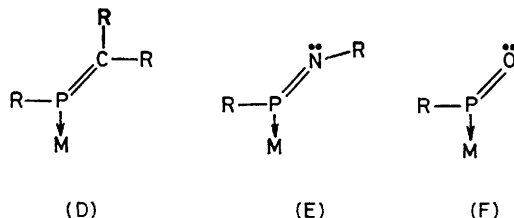
$RhCl(PPh_3)_3$  reacts with (**1**) to give the red-brown complex *trans*- $RhCl(PPh_3)_2[P(\text{mesityl})=CPh_2]$ , [ $^1J(\text{RhP})$  130.6,  $^1J(\text{RhPalkene})$  218.5,  $^2J(\text{PRhP}')$  54.9 Hz], while [ $RhCl(CO)_2$ ]<sub>2</sub> and (**1**) afford *trans*- $RhCl(CO)[P(\text{mesityl})-$



$=CPh_2]_2$ , [ $\nu(\text{CO})$  2000  $\text{cm}^{-1}$ ,  $^1J(\text{PRh})$  166 Hz]. The dark-red  $\eta^5$ -indenyl complex  $Rh(\eta^5-C_9H_7)[P(\text{mesityl})=CPh_2]_2$ , [ $^1J(\text{PRh})$  254 Hz] is readily formed by ethylene displacement from  $Rh(\eta^5-C_9H_7)(C_2H_4)_2$ .<sup>6</sup>

The platinum(II)-phospho-alkene complexes  $PtX_2[P(\text{mesityl})=CPh_2]_2$  (**3**) ( $X = Cl, I, Me$ ), are obtained from the corresponding cyclo-octadiene precursors [ $X = Cl$ ,  $^1J(\text{PtP})$  3950;  $X = I$ ,  $^1J(\text{PtP})$  4009;  $X = Me$ ,  $^1J(\text{PtP})$  1816 Hz]. Treatment of  $Pt_2Cl_4(\text{PET}_3)_2$  with (**1**) in  $CH_2Cl_2$  gives *trans*- $PtCl_2(\text{PET}_3)[P(\text{mesityl})=CPh_2]$ , as evidenced by its  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectrum [ $^1J(\text{PtPET}_3)$  2844,  $^1J(\text{PtPalkene})$  2590,  $^2J(\text{PPtP}')$  544 Hz], but removal of solvent followed by treatment with pentane gives yellow crystals of *cis*- $PtCl_2(\text{PET}_3)[P(\text{mesityl})=CPh_2]$ , [ $^1J(\text{PtPET}_3)$  3269,  $^1J(\text{PtPalkene})$  4294,  $^2J(\text{PPtP}')$  23 Hz].

$Pt_2Cl_4(\text{PET}_3)_2$  reacts with  $PCl(\text{mesityl})CHPh_2$  to give *trans*- $PtCl_2(\text{PET}_3)[PCl(\text{mesityl})(CHPh_2)]$ , but treatment of the latter with *dbu* did not induce HCl elimination to give  $PtCl_2(\text{PET}_3)[P(\text{mesityl})=CPh_2]$ , but instead gave *trans*- $PtCl_2(\text{PET}_3)(\text{dbu})$ . Likewise, several unsuccessful attempts were made to obtain  $CF_2=PH$  complexes *via* base-induced dehydrofluorination reactions of co-ordinated  $CF_3PH_2$ , *e.g.* using *cis*- $Mo(CO)_4(\text{PH}_2\text{CF}_3)_2$ .<sup>7</sup> Attempted synthesis of  $CF_3PH_2$  complexes of  $Pd^{II}$  and  $Pt^{II}$ , [as precursors for  $CF_2=PH$  complexes, *via* treatment of  $CF_3PH_2$  with  $M_2Cl_4(\text{PET}_3)_2$  ( $M = Pd, Pt$ )], gives instead novel dinuclear complexes  $Pd_2Cl_3(\text{PHCF}_3)(\text{PET}_3)_2$  and  $Pt_2Cl_2(\text{PHCF}_3)_2(\text{PET}_3)_2$  containing the bridging  $CF_3PH$  unit.



Our results on transition metal complexes of phospho-alkenes complement recent studies by Niecke and co-workers<sup>8</sup> on pentacarbonyl chromium complexes of iminophosphines,  $R^1PNR^2$ , and phosphinidene oxides,  $R^1PO$ , ( $R^1 = NPt_2$ ,  $R^2 = Bu^t$ ) and indicate that a common type of bonding obtains in these isoelectronic systems, *viz.* (D)—(F).

We thank the S.R.C. for financial support for this work.

(Received, 8th December 1980; Com. 1305.)

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