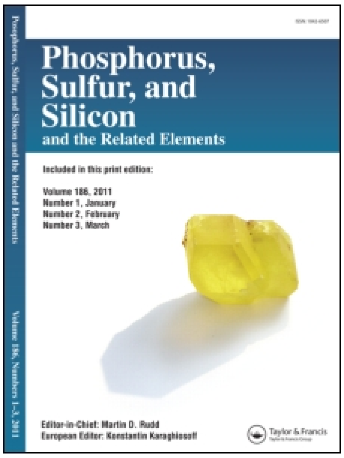

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# New Organorhodium and -Iridium Compounds of Iminophosphoranylmethanes

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# NEW ORGANORHODIUM AND -IRIDIUM COMPOUNDS OF IMINOPHOSPHORANYLMETHANES

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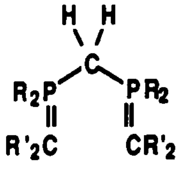
Abstract The synthesis and structure of new metallacyclic compounds of Rh(I) and Ir(I) containing bidentate mono- and bis(iminophosphoranyl)methane or -methanide ligands and their reactions with CO, phosphine and HCl are described.

## INTRODUCTION

The synthesis and reactivity of strongly polarized organophosphorus compounds containing *e.g.* P=C or P=N functionalities receive ample attention.[1] Compounds like **1** or **2** that comprise two such polar units, coupled by a methylene group, are known,[2,3] but their coordination and organometallic chemistry have hardly been investigated. Interestingly, *Roesky c.s.* recently published about a new complex **3** and its properties.[4] We have successfully focussed on the organometallic chemistry of bis(iminophosphoranyl)methane (bipm) ligands **2** with electron-rich late transition metal complexes, particularly $d^8$ metal centres. The synthesis and characterization of Rh(I) compounds **4a,c** and **5a,c** have been the subject of a preliminary report.[5]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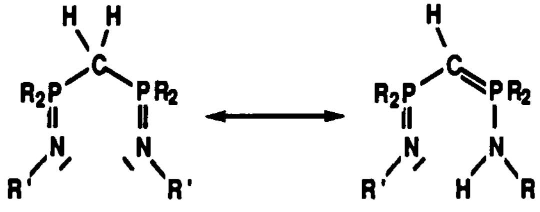
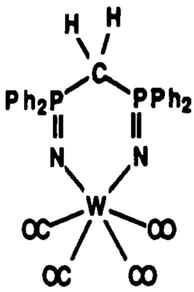

2a
2b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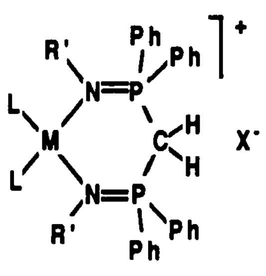
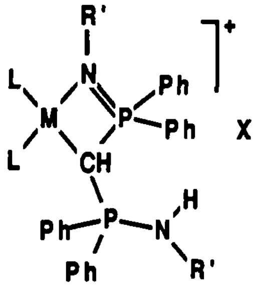

4a: M= Rh, $L_2$= COD; c: M= Rh, L= CO
b: M= Ir, $L_2$= COD; d: M= Ir, L= CO

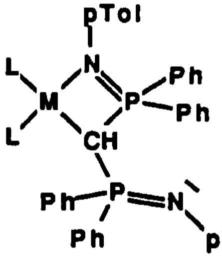

5a-d

In analogy with 1,3-diketones or bis(methylenephosphoranyl)methanes (**1**), bipm (**2**) may exist in tautomeric forms, although we could not establish the occurrence of measurable quantities of **2b** either in solution or in the solid state. It occurred to us, however, that it might be possible to stabilize tautomers of **2** *via* coordination to a transition metal fragment. Furthermore, one of the methylene hydrogens can easily be abstracted by base, providing access to an anionic ligand which is expected to exhibit good chelating properties toward transition metals, *e.g.* Rh(I) or Ir(I).

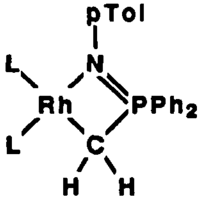
## SYNTHESIS AND STRUCTURE

The tautomeric forms of **2** were stabilized by coordinating the bipm ligand as a chelate to Rh(I)$^5$ and Ir(I). Novel metallacyclic compounds **4** and **5** could be isolated, in which $\sigma,\sigma$-N,N' and $\sigma$-N,$\sigma$-C chelate coordination, respectively, was established for the bipm ligands by multinuclear NMR spectroscopy. Upon reaction of $[ML_2Cl]_2$ (M=Rh, Ir; L=CO or $L_2$=COD) with $(4\text{-R-}C_6H_4\text{-N=PPh}_2)_2CH_2$ (R=$CH_3$, $OCH_3$, $NO_2$) in $C_6H_6$ or $CH_2Cl_2$ a mixture of complexes **4** and **5** is formed. The product ratio is strongly influenced by variation of the ancillary ligands L, *e.g.* for L = CO a 4/1 ratio **5**/**4** is obtained compared to 1/1 for $L_2$ = COD (M = Rh, R = $CH_3$, X = $[RhL_2Cl_2]$, benzene, 20 °C). This can be understood on the basis of the better $\pi$-acceptor properties of CO compared to COD, leading to the preferred isomer in which the better $\sigma$-donor (the carbanion) is in *trans*-position to the better $\pi$-acceptor. The proposed structures of **4a** and **5a** have been confirmed by X-ray diffraction studies.

During the formation of **5a**, one of the hydrogen atoms of the methylene group of **2** has shifted to one of the nitrogen atoms. This could be effected *via* cyclometallation by activation of one of the methylene C-H bonds of **2**, after which the abstracted H-atom migrates to either of the N-atoms. Another possibility would involve preferred direct coordination of tautomer **2b**, *i.e.* partial kinetic resolution of **2b**.



**6a**: M= Rh, $L_2$= COD; **c**: M= Rh, L= CO
**b**: M= Ir, $L_2$= COD; **d**: M= Ir, L= CO

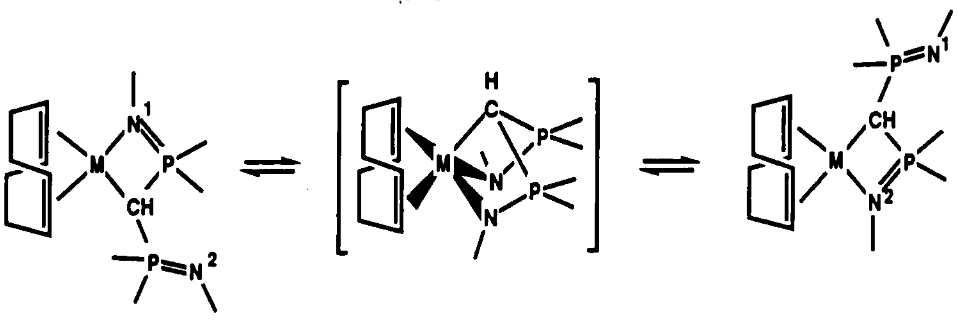


**7a, c**

New metallacyclic organorhodium(I) and -iridium(I) compounds **6** and **7** are obtained using organolithiumreagents of the type [{p-Tol-N=P(Ph)$_2$}$_2$CH-Li] or [p-Tol-N=P(Ph)$_2$-CH$_2$-Li] in reactions with [ML$_2$Cl]$_2$ (M=Rh, Ir; L=CO, L$_2$=COD). The molecular structure of compound **7a** (M=Rh, L$_2$=COD) has been confirmed by X-ray diffraction.

Compounds **5**, **6** and **7** are the first examples of *organometallic* derivatives of iminophosphoranylmethanes, which have in common that they contain a d$^8$-metal-to-sp$^3$-carbon bond. Interestingly, these Rh-C and Ir-C bonds are effectively stabilized by coordination of the nitrogen atom of the P=N moiety to the d$^8$ metal centre. The presence of the polar P=N entity induces polarization in the four-membered metallacycle, *i.e.* the M-C bond probably has considerable ionic character.

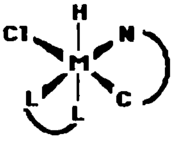
The solid-state $^{31}$P NMR of **6b** reveals the presence of two anisochronous P-atoms, as is expected on the basis of the X-ray data. The chemical shift values are very close together (20.0 and 22.5 ppm, respectively); one would have expected a larger difference. Possibly, delocalization over the P-C-P' unit plays a role. In solution also two $^{31}$P resonances would be expected. However, only one is observed at 17.9 ppm at temperatures between 353 and 193 K (at 2.35 Tesla), so apparently an exchange process occurs which is fast on the NMR timescale. A small difference in chemical shift for P and P' and/or a low activation energy for the exchange process could explain the fact that in toluene-d$_8$ at temperatures as low as 193 K (at 2.35 Tesla) still fast or intermediate exchange is observed. In the $^1$H NMR spectra only one signal is observed for the COD $\underline{H}$-C= protons (2.35 T; 193-353 K), so these inequivalent COD-sites are involved in chemical exchange as well. In view of these data the exchange process cannot involve breaking of the M-N$^1$ bond followed by rotation of the bipm ligand around M-C and formation of a M-N$^2$ bond. An exchange process in concert with all data is depicted below.



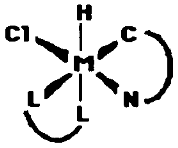
## REACTIVITY

Reaction of all complexes **5**, **6** and **7** with CO leads to clean displacement of the COD ligand by two CO molecules to give the bis-carbonyl products, Ph$_2$P-CH$_2$CH$_2$-PPh$_2$ (dppe) displaces the diene in **5a** to yield the dppe chelate. Neither of the compounds **5** - **7** are subject to insertion of CO (1-3 bar, 25 °C in C$_6$H$_6$ or CH$_2$Cl$_2$). This reluctance to undergo insertion of CO must be attributed to the presence of a highly polar M-C bond in and the rigidity *c.q.* stability of the metallacycle in **5**, **6** and **7**.

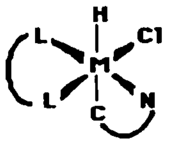
Reaction of **6a** or **6b** with HCl(g) gave **4a+5a** or **4b+5b**, respectively (X=Cl). The reaction may proceed *via* addition of HCl to the d$^8$-metal, yielding the d$^6$-complexes **8**, followed by a shift of the hydride H-atom to the coordinated N-atom and loss of Cl$^-$.



**8a**



**8b**



**8c**

This mechanism is corroborated by the observed conversion of **6b** into octahedral Ir-hydride compounds by reaction with HCl in toluene-$d_8$ at low temperature. The reaction could be followed by $^{31}$P and $^1$H NMR at 193 to 333 K; it appeared that three isomeric Ir-H compounds are involved. From the chemical shift position of the three hydride resonances (all at about -12 ppm) it can be concluded that these nuclei are in *trans* -position to carbon atoms in all cases, which observation leads to the formulation of complexes **8a** - **8c**. In these intermediates the H-atoms are in *cis* -position with respect to the N-atom (in **8a** - **8c**) and the methanide C-atom (in **8a**, **8b**), to which they can hence easily be transferred. Then, the other P=N moiety may coordinate to the metal. The products **4** and **5** are also formed in the direct reaction of bipm with [M$^I$L$_2$Cl]$_2$, but it remains to be seen whether metal hydrides are intermediates in that reaction.

## ACKNOWLEDGEMENT

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