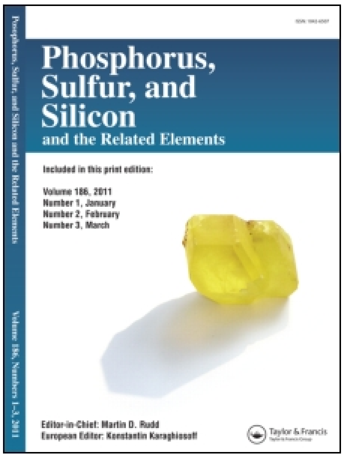

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Synthesis and Reactivity of Transition Metal Phosphoranides Having Three-Membered Phosphorus-Metal Nitrogen (or Oxygen) Rings

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SYNTHESIS AND REACTIVITY OF TRANSITION METAL PHOSPHORANIDES HAVING THREE-MEMBERED PHOSPHORUS-METAL NITROGEN (OR OXYGEN) RINGS

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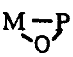
Abstract An account of our research on the synthesis and reactivity of transition metal phosphoranides having three-membered phosphorus-metal-nitrogen (or oxygen) ring is given. An attempt at acceding to acyclic phosphoranide complexes from $LiNR_2$ and $CpFeL^1L^2X$ derivatives (L^1 = CO, L^2 = PR_3; L^1 = L^2 =PR_3; X = Cl, Br) resulted in the direct amination of the cyclopentadienyl ring. The influence of R, L and X on the issue of the reaction is discussed.

Our search for transition metal phosphoranides (or metallophosphoranes) followed an investigation of the equilibrium between bicyclic hydroaminophosphoranes **1** and their monocyclic phosphane/amine tautomers **1'**. It was shown that the latter, usually undetected form **1'**, readily coordinates transition metals either via the phosphorus atom alone (as in **2**) or via both the phosphorus and nitrogen atoms (as in **3**).[1]

These findings raised the question whether a similar tautomeric transformation could operate between the deprotonated coordinated forms **4** and **5**, i.e. the amido-phosphane chelate and phosphoranide adduct, respectively. The "intramolecular-intraligand" P-N bond closing process was observed to occur and led us to obtain in high yields the hitherto unknown coordination compounds of type **5** (M = Mo, W; R = Ph)[2] in which a phosphoranide anion behaves as a ligand toward a metal. This approach has since been applied successfully to the synthesis of the Fe and Ru phenylphosphoranides[3], of related benzyl, methyl, vinyl, allylphosphoranides[4] and of cyclamphosphoranides.[5]

The unusual structural features of phosphoranides **5**, in addition to the presence of a metal among the five substituents of the phosphorus atom, are the coordination of a phosphorus-bound nitrogen atom, i.e. the occurence of a $\overset{N}{M - P}$

cycle, and its thermal isomerisation to phosphoranide 6, i.e. the occurence of the  cycle.[6]

The strong M - N bond in 5, despite the nitrogen being bonded to the π-acid phosphorus atom, is also noteworthy. De-coordination of this nitrogen could not be achieved under the action of CO, PPh_3 or PMe_3; neither 11 nor 12 were observed to form.

On the other hand, the iron phenylphosphoranide 5 is converted into the phenyliron phosphane adduct 7, as a result of the unexpected migration of the phenyl group from phosphorus to iron. This migration can be reversed quantitatively under the action of gaseous HCl on 7 to give back the cationic phenylphosphane derivative 3. A chemical labeling of the phenyl ring ($Ph^{\bullet}$) allowed us to show that it is the same carbon atom of the phenyl group that is alternately bounded to phosphorus and to iron, thus excluding an orthometalation pathway and establishing a 1,2-sigmatropic shift mechanism for this migration.[3]

This process exemplifies a metal-induced interconversion between a hypervalent (1) and a "normavalent" (18) phosphorus derivative. It also raises the question whether or not such metal-phosphoranides play a more general role as intermediates in P-C bond rupture processes.

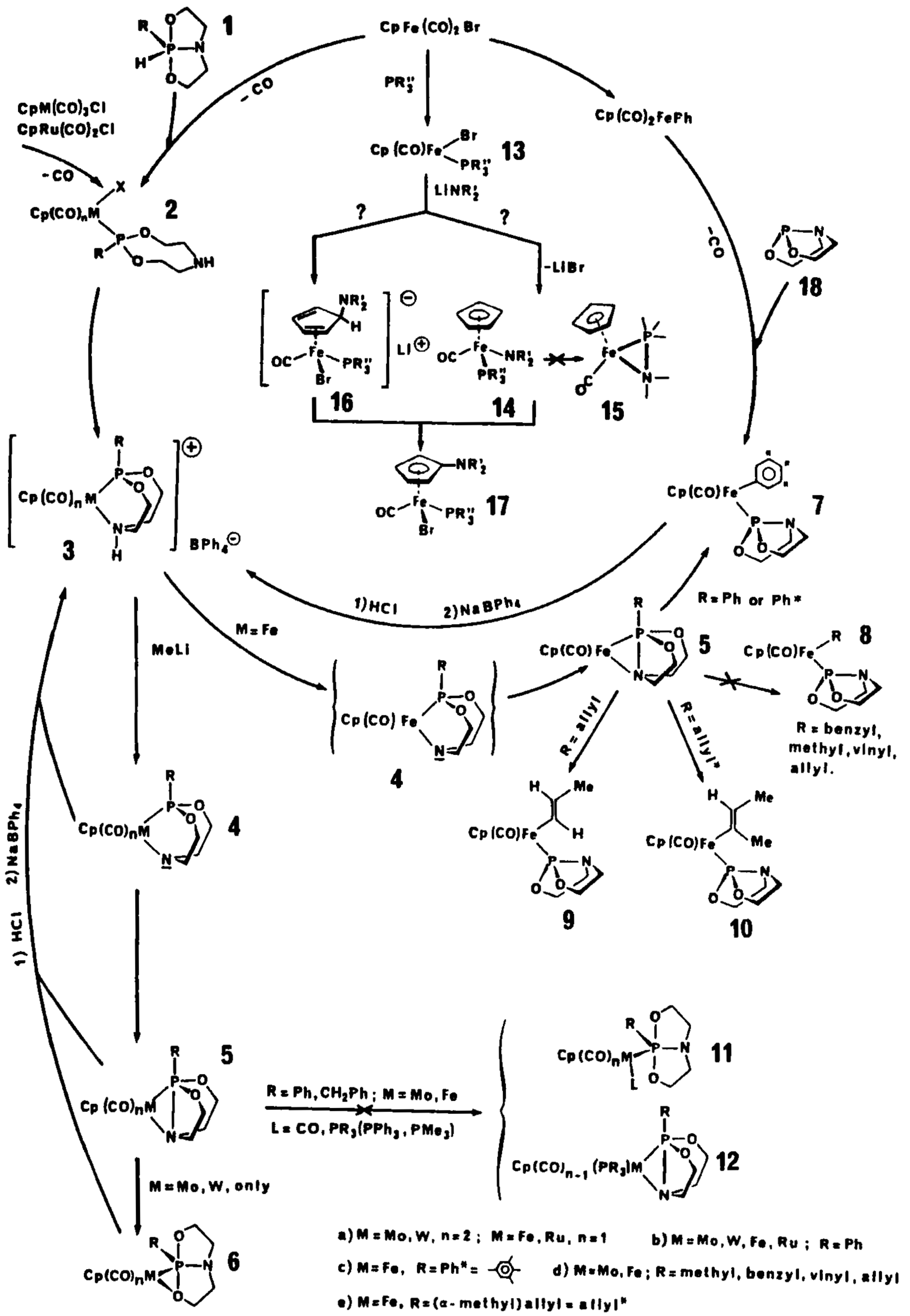
As we explored the possibility of taking advantage of this migration process for forming M-C bonds, a novel reactivity was found with the iron allylicphosphoranides 5 (R = allyl, allyl*) which did not yield the expected σ-allylic iron adducts 8, but the rearranged σ-vinylic iron complexes 9 and 10 respectively.[4] These transformations are stereoselective, since 9 and 10 are formed respectively in a trans and cis configuration at the double bond. Chemical labeling of the allyl group in 5 (R = allyl*) established that the P-allylic to Fe-vinylic conversion proceeds through insertion of the iron atom into an allylic C-H bond, followed by a 1,3 proton shift to the terminal olefinic carbon atom, with concomitant P-C bond cleavage. This reactivity pattern differs both from the phenyl group migration, which implies only P-C bond rupture, and from an orthometalation reaction, which implies only insertion of the metal into a C-H bond.[4]

Despite extensive investigations, no phenyl migration was detected when similar conditions were applied to the Ru, Mo and W phenylphosphoranides,[3] while complex reactions were observed in the case of the iron benzyl, vinyl or methylphosphoranides **5**.[4]

The interesting new behaviors described above led us to explore an "intramolecular-interligand" reaction as a possible access to the acyclic phosphoranide complexes of type **15**. But, instead of the expected product, this approach provided a new, direct access to the aminocyclopentadienyl ($C_5H_4NR_2$) iron complexes **17**.[8] Although cyclopentadienyl compounds have found wide applications as ligands in organometallic chemistry, few cyclopentadienylamines ($C_5H_4NR_2$) and even fewer of their complexes are known compared to other functionnalized cyclopentadienyl rings. This led thus to the question whether, and to what extend, this Cp ring amination reaction could be developed into a general method . The action of $LiNR_2$ on various $CpFeL^1L^2X$ derivatives (L^1 = CO, L^2 = PR_3; L^1 = L^2 = PR_3; X = Cl, Br) has therefore been investigated and showed that the issue of these reactions strongly depends on the nature of R, L and X : (i) it leads to $C_5H_4NR_2$ adducts only when $R \neq H$; (ii) the steric and π-accepting properties of the phosphorus ligands L favor the amination process: CpFe(CO)LX or $CpFeL_2X$ give higher yields in **17** than $CpFe(CO)_2X$ while the reaction does'nt take place with CpFe(dppe)Br for example; (iii) the brominated derivatives **13** are much better starting materials than their chlorinated analogues.

References

1. C. Pradat, J.G. Riess, D. Bondoux, B.F. Mentzen, I. Tkatchenko, D. Houalla, J.Am.Chem.Soc., 101, 2234 (1979).
2. F. Jeanneaux, A. Grand, J.G. Riess, J.Am.Chem.Soc., 103, 4272 (1981).
3. P. Vierling, A. Grand, J.G. Riess, J.Am.Chem.Soc., 103, 2466 (1981); Inorg.Chem. in the press.
4. P. Vierling, J.G. Riess, J.Am.Chem.Soc., 106, 2432 (1984); Organometallics, 5, xxxx (1986).
5. J.-M. Dupart, A. Grand, S. Pace, J.G. Riess, J.Am. Chem.Soc., 104, 2316 (1982).
6. J. Wachter, B.F. Mentzen, J.G. Riess, Angew.Chem. Int.Ed.Engl. , 20, 284 (1981).
7. J. Hartgerink, P. Vierling, J.G. Riess, G. Le Borgne, G. Nouv.J.Chim., 9, 707 (1985). P. Brun, P. Vierling, J.G. Riess, submitted.



a) M = Mo, W, n = 2 ; M = Fe, Ru, n = 1 b) M = Mo, W, Fe, Ru ; R = Ph

c) M = Fe, R = Ph* = d) M = Mo, Fe ; R = methyl, benzyl, vinyl, allyl

e) M = Fe, R = (α-methyl)allyl = allyl*