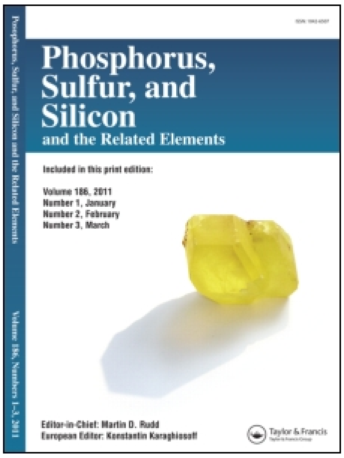

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Phosphinines and Diphosphaferrocenes: Recent Advances

Patrick Rosa[a]; Xavier Sava[a]; Nicolas Mézailles[a]; Mohand Melaimi[a]; Louis Ricard[a]; François Mathey[a]; Pascal Le Floch[a]
[a] Laboratoire "Hétéroéléments et Coordination,", Ecole Polytechnique, Palaiseau Cedex, France

To cite this Article Rosa, Patrick , Sava, Xavier , Mézailles, Nicolas , Melaimi, Mohand , Ricard, Louis , Mathey, François and Floch, Pascal Le(2002) 'Phosphinines and Diphosphaferrocenes: Recent Advances', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1529 — 1532

To link to this Article: DOI: 10.1080/10426500212220

URL: http://dx.doi.org/10.1080/10426500212220

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1529–1532

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290092695

PHOSPHININES AND DIPHOSPHAFERROCENES: RECENT ADVANCES

*Patrick Rosa, Xavier Sava, Nicolas Mézailles, Mohand Melaimi,
Louis Ricard, François Mathey, and Pascal Le Floch
Laboratoire "Hétéroéléments et Coordination," Ecole
Polytechnique, Palaiseau Cedex, France*

(Received July 30, 2001; accepted December 25, 2001)

Recent developments in the chemistry of phosphinines and phosphaferrocenes are reviewed. Phosphinine-based macrocycles such as silacalix-[4]-phosphinines efficiently stabilize gold(0). 2,2′Biphosphinines which behave as powerful chelates show a greater ability than their nitrogen counterparts for the stabilization of highly reduced and electron-excessive transition metal centers. On the other hand, diphosphaferrocenes coordinate various metal centers via a side-on bonding mode. Palladium(0) complexes of octa-alkyl diphosphaferrocenes behave as efficient catalysts both in the Suzuki cross-coupling reaction and in the synthesis of arylboronic esters.

Keywords: Macrocycles; phosphaferrocenes; phosphinines

Dicoordinate phosphorus compounds show unusual electronic and structural features that render them very different from classical tertiary phosphines and classical nitrogen *sp*^{2}-based derivatives.[1] As a result of the lower electronegativity of phosphorus with regards to nitrogen, dicoordinated P compounds usually possess low-lying LUMOs. This characteristic makes them very attractive ligands for the coordination of electron-rich metal centers. A second important feature, which is related to the weaker hybridization of phosphorus orbitals, concerns the presence of a very diffuse lone pair at phosphorus that shows an important 3*s* character. Over the last few years, we mainly investigated the use of *sp*^{2}-based phosphorus heterocyles in coordination chemistry and catalysis. In this article we report on the more interesting advances.

RESULTS AND DISCUSSION

Phosphinine-based macrocyles such as silacalix-[*n*]-phosphinines can be regarded as phosphorus equivalents of CO matrices.[2] The most

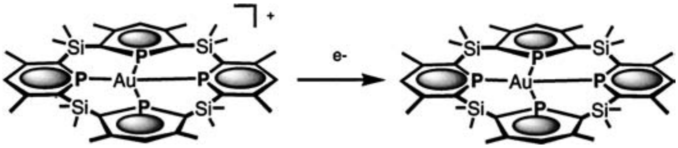

FIGURE 1

significant example was provided by the stabilization of a Au(0) complex of the silacalix-[4] macrocycle. The monolectronic reduction of the corresponding Au(I) complex yields the Au(0) complex, which was unambiguously characterized by electron paramagnetic resonance (EPR) spectroscopy.[3] Contrary to what observed with $Au(CO)_n$ and $Au(C_2H_4)_n$, which were characterized in matrices and decompose when the temperature reaches 15 K, this macrocyclic derivative is stable up to 240 K (Figure 1).

Interesting advances were also achieved with 2,2′-biphosphinines,[4] the phosphorus equivalents of the ubiquitous 2,2′-bipyridines. Contrary to their nitrogen counterparts, these ligands can efficiently stabilize highly reduced transition metal centers such as Zr, Ti and Hf(2−),[5] Mn(−1), Fe, Ru(2−),[6] Co, Rh(−1), Pt(2−), and Ni(−1). Most of these complexes were obtained by reacting the reduced ligand with the appropriate metallic salts. The synthesis of the homoleptic group 4 dianionic complexes is illustrated in Figure 2.

Theoretical calculations carried out on the Ru(2−) complex reveal that a significant part of the electron density resides on the two biphosphinine ligands. Thus, this Ru(2−) species can be regarded as the coordination of two monoanionic biphosphinines to an Ru(0) center. This very specific electron distribution accounts for the unusual square planar geometry generally associated with transition metal centers having the d^8 electronic configuration.[6]

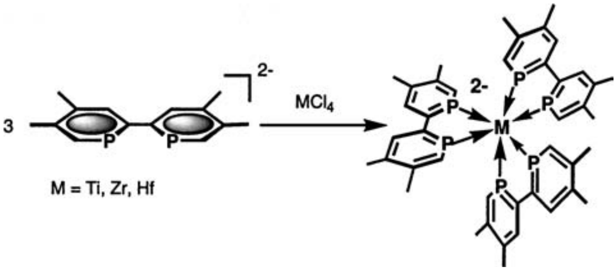

FIGURE 2

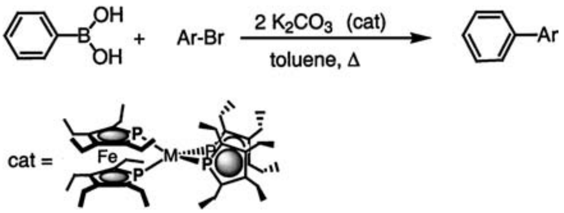

FIGURE 3

Diphosphaferrocenes also show unusual electronic and structural properties. The combination of the ferrocenyl backbone and the sphericity of the phosphorus atom lone pair can be exploited to develop a surprising coordination chemistry. Thus, chelate complexes adopt an unusual side-on bonding mode in which the metal centers are weakly bound to the phosphorus atoms. This very particular bonding allows the building of sophisticated polymetallic edifices incorporating several diphosphaferrocenes units. Another interesting mechanical consequence is provided by the hemilabile character of the ligand. This property can be exploited to devise an efficient catalyst. A striking illustration was given in the palladium-catalyzed Suzuki cross-coupling reaction (Figure 3). The bis(octatehyldiphosphaferrocene) Pd(0) derivative catalyzes the Suzuki cross-coupling reaction between phenylboronic acid and various bromoarenes with excellent Turn Over Number (TON) up to 1×10^6.[7]

A second interesting result was obtained by studying the palladium Myaura cross-coupling process, which allows the preparation of arylboronic esters (Figure 4). The use of a bimetallic Pd(II) complex leads to a quantitative conversion yield and high TON (up to 3×10^3, compared to 33 for the usual systems).[8]

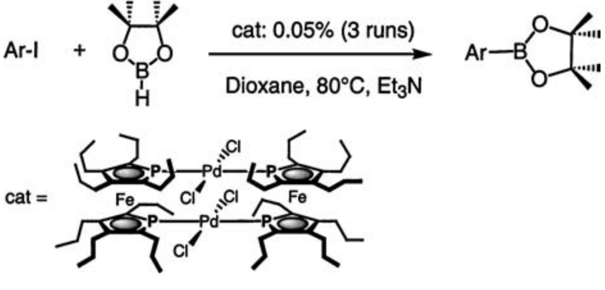

FIGURE 4

REFERENCES

[1] K. B. Dillon, F. Mathey, and J. F. Nixon, In *Phosphorus: The Carbon Copy* (Wiley, Chichester, 1998).

[2] N. Avarvari, N. Mézailles, L. Ricard, P. Le Floch, and F. Mathey, *Science*, **8,** 1587 (1998).

[3] N. Mézailles, N. Avarvari, N. Maigrot, L. Ricard, F. Mathey, P. Le Floch, L. Cataldo, T. Berclaz, and M. Geoffroy, *Angew. Chem. Int. Ed. Engl.*, **21,** 3194 (1999).

[4] N. Mézailles, F. Mathey, and P. le Floch, *Prog. Inorg. Chem.*, **49,** 455 (2001).

[5] P. Rosa, N. Mézailles, L. Ricard, F. Mathey, and P. Le Floch, *Angew. Chem. Int. Ed. Engl.*, **39,** 1823 (2000).

[6] P. Rosa, N. Mézailles, L. Ricard, F. Mathey, P. Le Floch, and Y. Jean, *Angew. Chem. Int. Ed. Engl.*, **40,** 1251 (2000).

[7] X. Sava, L. Ricard, F. Mathey, and P. Le Floch, *Organometallics*, **19,** 5247 (2000).

[8] M. Melaimi, F. Mathey, and P. Le Floch, *S. Organomet. Chem.*, **640,** 197 (2001).