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The α-Iminophospholide Ligands

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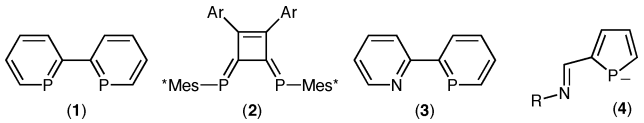
Ligands incorporating a delocalized −N=C−C=N− core (e.g., 2,2′-bipyridines and 1,4-diazadienes) play a central role in coordination chemistry and homogeneous catalysis. The analogous −P=C−C=P− ligands have also been studied to some extent. 2,2′-Biphosphinines (**1**) display strong π-accepting properties and stabilize transition metal centers in low oxidation states.[1] Stabilized 1,4-diphosphadienes, such as **2**, have already found some interesting catalytic applications.[2] The dissymmetrical −P=C−C=N− ligands are only represented today by 2,2′-pyridylphosphinines (**3**).[3] Their chemistry is rather disappointing because the two subunits behave independently. This finding can be easily rationalized if we consider the electronic properties of imines and phosphaalkenes. The π-bond of H_2C=NH appears at −12.49 eV, whereas the π-bond of H_2C=PH is much higher in energy at −10.30 eV.[4] This huge gap prevents any sizable delocalization within a −P=C−C=N− unit. To restore some cooperativity between the sp^2-N and sp^2-P centers, the simplest option is to stabilize the P=C double bond by incorporation into an aromatic ring. This led us to consider the α-iminophospholide ions (**4**) as a potential solution.



An additional interest of these ligands lies in their analogy with the well-known α-iminopyrrolides, whose applications in polymerization catalysis have been studied in some depth recently.[5]

To get a more precise idea of the electronic properties of such P,N-ligands, we first decided to perform a DFT study of a representative species **5** with Li^+ as the counterion at the B3LYP/6-311++G(3df,2p) level of theory.[6] The computed structure is shown in Figure 1.

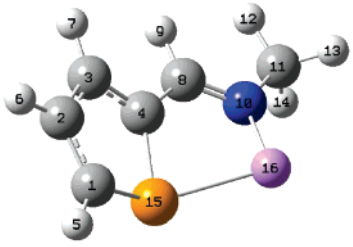
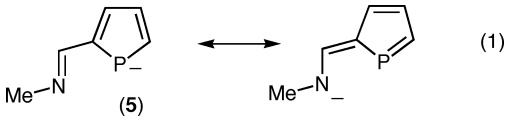


Figure 1. Computed structure of lithium 2-(*N*-methylimino)phospholide (**5**). Main bond lengths (Å) and angles (deg): P−C1 1.742, P−C4 1.795, C1−C2 1.395, C2−C3 1.396, C3−C4 1.404, C4−C8 1.426, C8−N 1.299, P−Li 2.366, N−Li 1.914; C1−P−C4 90.33, P−C4−C8 126.26, C4−C8−N 124.26, N−Li−P 98.70, P−C4−C8−N 16.40.

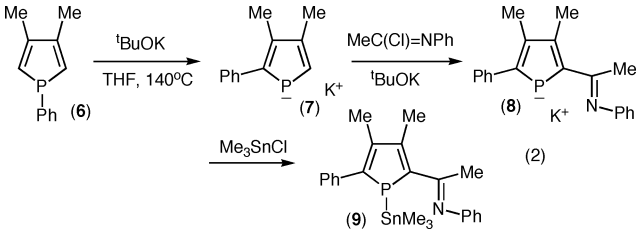
The lithium ion is not η^5-coordinated to the phosphole ring as in nonfunctional phospholides[7] but chelated between phosphorus and nitrogen. The structure of the ligand is essentially planar except for a slight displacement of the imino nitrogen away from the plane on the same side as lithium (P−C4−C8−N dihedral angle = 16.4°).

From these data (especially the short C2−C3 bond at 1.396 Å, and the significantly contracted P−C1 bond at 1.742 Å), it is quite clear that the electronic structure of **5** is better represented by a mesomeric formulation (eq 1).



A NBO analysis fully confirms this point: charge at P +0.236, charge at N −0.694 e. Thus, the nitrogen will be the donor and phosphorus the acceptor center. This theoretical study clearly establishes the full cooperativity between the two sp^2-coordinating centers of **5**.

The synthesis of α-iminopyrrolides cannot be transposed for obtaining α-iminophospholides. However, some time ago, we described a simple method which converts α-unsubstituted into α-functional phospholides using a [1,5] shift of the functional group from P to C_α.[8] We thus studied the reaction of phospholides with imidoyl chlorides.[9] The chemistry is described in eq 2.



The α-phenyl group has been introduced for steric protection of the phosphorus coordinating center. The α-iminophospholide (**8**) gives a ^{31}P resonance at 87.8 ppm in THF. The reaction with trimethyltin chloride gives **9**,[10] which can be isolated by crystallization. The overall yield of **9** from **6** can reach 40%. The X-ray crystal structure of **9** is shown in Figure 2).

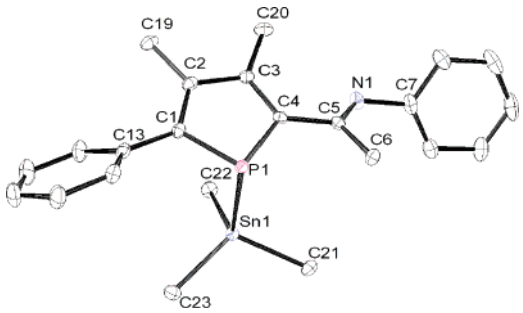


Figure 2. X-ray crystal structure of phosphole **9**. Main bond lengths (Å) and angles (deg): P1−Sn1 2.5349(8), P1−C1 1.795(3), P1−C4 1.803(3), C1−C2 1.372(4), C2−C3 1.455(4), C3−C4 1.377(4), C4−C5 1.473(4), C5−N1 1.284(3); C1−P1−Sn1 95.51(9), C4−P1−Sn1 95.80(9), C1−P1−C4 90.44(12), P1−C4−C5 121.39(19), C4−C5−N1 119.2.

10.1021/ja060100q CCC: $33.50

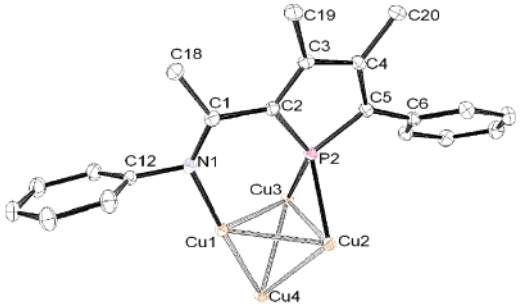


Figure 3. Ligand structure in copper complex **10**. Selected bond lengths (Å): P2−C5 1.7557(16), P2−C2 1.7760(16), N1−C1 1.296(2), N1−C12 1.433(2), C1−C2 1.457(2), C1−C18 1.509(2), C2−C3 1.405(2), C3−C4 1.421(2), C3−C19 1.512(2), C4−C5 1.393(2), C4−C20 1.512(2), C5−C6 1.477(2), C6−C11 1.398(2), C6−C7 1.399(2), C7−C8 1.389(2), C8−C9 1.387(2), C9−C10 1.383(3), C10−C11 1.393(2), C12−C13 1.390(2), C12−C17 1.390(2), C13−C14 1.387(2), C14−C15 1.387(3), C15−C16 1.383-(3), C16−C17 1.390(2), Cu1−Cu2 2.6046(3), Cu1−Cu3 2.7041(3), Cu1−Cu4 2.5495(3), Cu2−Cu3 2.5691(3), Cu2−Cu4 2.7330(3), Cu3−Cu4 2.6101(3).

The structure is characterized by the *E* stereochemistry at the C═N double bond, probably for steric reasons, a highly pyramidal phosphorus atom (sum of the angles at P = 281.7°) and a very low delocalization within the ring. In fact, this is the most pyramidal phosphole whose structure has been recorded to date.[11] Stannylphosphole (**9**) is a convenient precursor for the transition metal complexes of the α-iminophospholide (**8**). As an example, its reaction with copper(I) chloride leads to a red diamagnetic tetrameric complex $[Cu(\mathbf{8})]_4$ (**10**) in 92% yield.[12] The iminophospholide acts as a bridging five-electron μ_2-P, η^1-N-ligand as shown in Figure 3). Each copper atom has 16 electrons in its valence shell if we ignore the copper−copper bonds. Thus, clusterization takes place to bring the electron count up to 18 electrons. It is interesting to compare this situation to that found in the other structurally characterized copper−phosphide complex $[Cu(phen)(PPh_2)]_3$, where the 18e rule is fulfilled without metal−metal bonds.[13] Broadly speaking, the structure of the ligand in **10** is intermediate between those of **5** and **9**. This means that some delocalization is still effective in **10**. It is anticipated that tuning the steric bulk of the nitrogen substituent of **8** will permit the isolation of interesting monomeric electron-deficient complexes.

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Supporting Information Available: Complete ref 6. X-ray crystal structure analysis of compounds **9** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) A solution of 1-phenyl-3,4-dimethylphosphole (2 mL, 10 mmol) in tetrahydrofuran (40 mL) and ^{t}BuOK (1.23 g, 11 mmol) was freeze−thaw−degassed twice in a thick-walled glass ampule sealed with a Teflon valve. The mixture was heated (under a static vacuum) to 140 °C for 8 h. Volatiles were removed in vacuo, then the mixture was redissolved in tetrahydrofuran (40 mL), cooled to −78 °C, and *N*-phenylacetimidoyl chloride (15 mmol, 2.3 g, 2.01 mL) added via syringe. After the solution was allowed to warm to ambient temperature, it was stirred for 30 min, then ^{t}BuOK (1.12 g, 10 mmol) was added and warmed to 40 °C for 1 h, then cooled to 0 °C, and trimethyltin chloride (2.1 g, 11 mmol) added. The mixture was stirred for 1 h, then volatiles were removed in vacuo. The product was extracted with hexane (3 × 20 mL) and crystallized from hexane to give pale yellow crystals of pure phosphole **9** (40% yield, 1.86 g): ^{31}P NMR $CDCl_3$ δ −46.4 ($^1J_{PSn}$ = 552 Hz); ^{1}H NMR $CDCl_3$ δ 7.30−7.15 (m, C_6H_5), 6.96 (1H, m, *Ph*), 6.69 (2H, m, *Ph*), 2.39 (3H, d, $^4J_{PH}$ = 1.6 Hz, $^5J_{SnH}$ = 17 Hz, CH_3), 2.17 (3H, d, $^4J_{PH}$ = 1.6 Hz, $^5J_{SnH}$ = 14 Hz, CH_3), 2.08 (3H, d, $^4J_{PH}$ = 1.2 Hz, CH_3), −0.08 (9H, d, $^3J_{PH}$ = 2.1, $^2J_{SnH}$ = 49.2, SnCH_3); ^{13}C NMR $CDCl_3$ δ 165.9 (*C*═N), 153.11 (C_{ipso}-Ph), 151.8 (P$C_{(ring)}$), 148.1 (PC$C_{(ring)}$), 146.3 (P$C_{(ring)}$), 142.2 (PC$C_{(ring)}$), 138.6 (C_{ipso}Ph), 129.1 (C_6H_5), 129.0 (C_6H_5), 128.3 (C_6H_5), 126.5 (C_6H_5), 122.8 (C_6H_5), 119.7 (C_6H_5), 22.5 (d, $^3J_{PC}$ = 7.3 Hz, *C*H$_3$), 16.6 (*C*H$_3$), 15.1 (*C*H$_3$), −8.5 (d, Sn(*C*H$_3$)$_3$, $^3J_{PC}$ = 5.5 Hz, $^2J_{SnC}$ = 312 Hz).

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(12) A solution of phosphole **9** (1.15 mmol, 0.54 g) in dichloromethane (10 mL) was added dropwise to a suspension of CuCl (1.15 mmol, 0.11 g) in dichloromethane (20 mL) at 0 °C. The mixture was allowed to warm to ambient temperature and stirred for 8 h. The resulting red solution was dried in vacuo, then redissolved in dichloromethane. The solution was kept at −5 °C for 8 h, resulting in the formation of pure red crystals of the tetrameric complex **10** (92%, 0.48 g): ^{31}P NMR C_6D_6 δ −128.0; ^{1}H NMR C_6D_6 δ 7.23−6.73 (m, C_6H_5), 6.76 (1H, m, *Ph*), 6.69 (2H, m, *Ph*), 2.37 (3H), 2.34 (3H), 1.88 (3H); ^{13}C NMR C_6D_6 δ 169.5 (*C*═N), 149.4 (PC$C_{(ring)}$), 141.4 (P$C_{(ring)}$), 138.8 (P$C_{(ring)}$), 133.1 (C_6H_5), 131.4 (C_6H_5), 126.7 (C_6H_5), 124.9 (C_6H_5), 124.9 (C_6H_5), 124.1 (C_6H_5), 124.1 (C_6H_5), 123.1 (C_6H_5), 22.8 (*C*H$_3$), 19.3 (*C*H$_3$), 15.7 (*C*H$_3$).

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