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Boosting the Nucleophilicity of Phosphole Lone Pairs by Isomerization†

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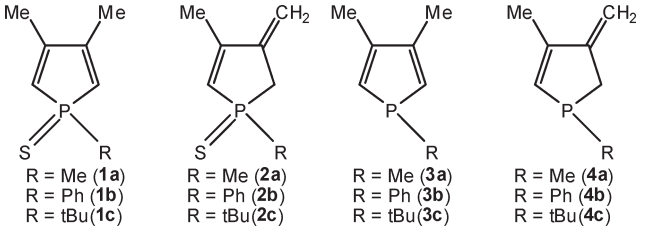
Summary: The phosphole isomer ***4c*** *can be obtained by nickelocene reduction complexation from the corresponding sulfide. It displays a ligating ability comparable to that of tris-tert-butylphosphine, and its* $[LPdCl_2]_2$ *complex efficiently catalyzes the deboronation homocoupling of arylboronic acids.*

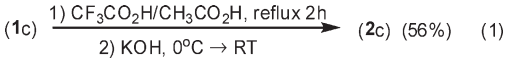
Due to their slight antiaromaticity,[1] phosphole sulfides such as **1a** tend to isomerize to give products such as **2a** with one exocyclic double bond.[2] Since phospholes are slightly aromatic, the tendency is inverted for the trivalent species. DFT calculations at the B3LYP/6-311+G(d,p) level perfectly confirm these trends: **2a** is more stable than **1a** by 2.4 kcal mol^{-1}, whereas **4a** is less stable than **3a** by 3.5 kcal mol^{-1}.



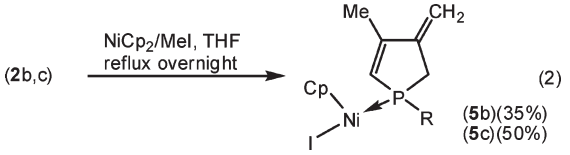
A closer inspection of the theoretical data showed that the lone pair at phosphorus is shifted to higher energy by 0.49 eV upon isomerization of **3a** into **4a**. This destabilization of the lone pair is probably due to an antibonding overlap with the HOMO of the diene unit as shown in Figure 1, although other factors such as geometry changes and hyperconjugation with the neighboring CH_2 group might also intervene. It must be stressed here that 2-phospholenes should also be electron-rich ligands for reasons similar to those already mentioned.[3] When **4a** is compared with **4c**, the replacement of Me by tBu leads to a further increase of the lone pair energy by 0.11 eV.

In fact, the lone pair of **4c** appears at the same energy as the lone pair of tri-*tert*-butylphosphine. Obviously, these phosphole isomers deserved an experimental investigation.

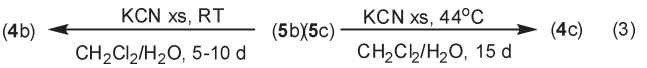
Our starting products were the two isomeric sulfides **2b**,**c**. Compound **2b** has already been described in the literature.[2] The previously unknown **2c**[4] was made by acidic isomerization of the corresponding phosphole sulfide following an early protocol[2] (eq 1).



The desulfurization of **2c** by sodium in boiling toluene did not give satisfactory results; thus, we decided to use a mild technique relying on the reduction−complexation of *P*-sulfides by nickelocene.[5] Being driven by the complexation ability of the P ligand, this method efficiently reduces **2**, whereas it fails with **1** (eq 2). The 1:1 P:Ni complexes thus obtained were fully characterized,[6] including X-ray crystal structure analyses.



The decomplexation was performed by KCN in H_2O/CH_2Cl_2. It takes several days for completion (eq 3).



As expected, the conditions are more drastic for **4c** than for **4b**, implying that the corresponding phosphole isomer **3c** is a

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(4) **2c**: ^{31}P NMR ($CDCl_3$) δ 73.8; ^1H NMR ($CDCl_3$) δ 1.20 (d, J_{HP} = 17 Hz, tBu), 2.03 (s, Me), 2.81 (pseudo t, 1H, $J_{HH} \approx J_{HP} \approx 17$ Hz, CH_2P), 3.15 (dd, 1H, J_{HH} = 17.9 Hz, J_{HP} = 5.5 Hz, CH_2P), 5.16 (s br, 1H, $=CH_2$), 5.25 (s br, 1H, $=CH_2$), 5.94 (d, J_{HP} = 24.3 Hz, =CHP); ^{13}C NMR ($CDCl_3$) δ 16.48 (d, J_{CP} = 16.2 Hz, Me), 24.69 (s, Me (tBu)), 33.90 (d, J_{CP} = 51.5 Hz, CH_2P), 34.99 (d, J_{CP} = 50.6 Hz, C(tBu)), 112.02 (d, J_{CP} = 12.4 Hz, $=CH_2$), 124.70 (d, J_{CP} = 69.6 Hz, =CHP), 145.92 (d, J_{CP} = 7.6 Hz, C=), 156.42 (d, J_{CP} = 10.5 Hz, =C).

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(6) **5b**: ^{31}P NMR ($CDCl_3$) δ 35.5; ^1H NMR ($CDCl_3$) δ 2.08 (s, Me), 2.97 (dd, 1H, J_{HH} = 17.4 Hz, J_{HP} = 10 Hz, CH_2P), 3.52 (d, 1H, J_{HH} = 17.4 Hz, J_{HP} = 0 Hz, CH_2P), 5.21 and 5.33 (2s, 2 × 1H, $=CH_2$), 5.40 (s, Cp), 6.14 (d, J_{HP} = 29.8 Hz, =CHP), 7.41 (s br, *m*,*p*-Ph), 7.91 (m, *o*-Ph); ^{13}C NMR ($CDCl_3$) δ 16.70 (d, J_{CP} = 11.5 Hz, Me), 38.61 (d, J_{CP} = 36.3 Hz, CH_2P), 93.35 (s, Cp), 111.56 (d, J_{CP} = 8.6 Hz, $=CH_2$), 128.64 (d, J_{CP} = 10.5 Hz, CH(Ph)), 129.43 (d, J_{CP} = 43.9 Hz, =CHP), 130.96 (s, *p*-CH(Ph)), 132.93 (d, J_{CP} = 12.4 Hz, CH(Ph)), 135.36 (d, J_{CP} = 40.1 Hz, *ipso*-C(Ph)), 148.89 (s, =C), 153.70 (d, J_{CP} = 4.8 Hz, =C). **5c**: ^{31}P NMR ($CDCl_3$) δ 57.2; ^1H NMR ($CDCl_3$) δ 1.16 (d, J_{HP} = 15 Hz, tBu), 1.97 (s, Me), 2.80 (dd, 1H, J_{HH} = 17.4 Hz, J_{HP} = 7.3 Hz, CH_2P), 3.19 (d br, 1H, J_{HH} = 17.4 Hz, J_{HP} = 0 Hz, CH_2P), 5.14 and 5.20 (2s, 2 × 1H, $=CH_2$), 5.34 (s, Cp), 5.97 (d, J_{HP} = 28.8 Hz, =CHP); ^{13}C NMR ($CDCl_3$) δ 16.57 (d, J_{CP} = 10.5 Hz, Me), 27.41 (d, J_{CP} = 3.8 Hz, Me(tBu)), 32.94 (d, J_{CP} = 31.6 Hz, CH_2P), 34.58 (d, J_{CP} = 22 Hz, C(tBu)), 93.27 (s, Cp), 110.43 (d, J_{CP} = 7.7 Hz, $=CH_2$), 128.14 (d, J_{CP} = 38.3 Hz, =CHP), 149.50 (s, =C), 153.16 (s, =C).

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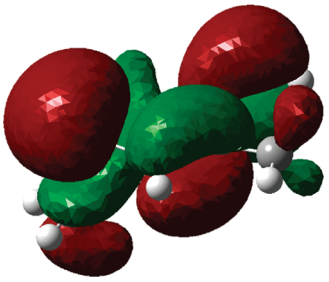
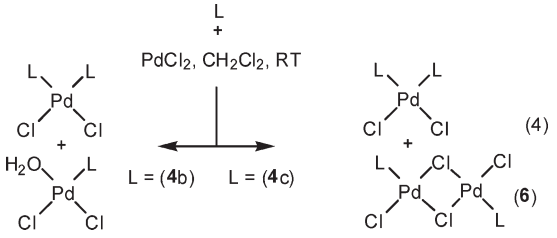


Figure 1. Highest occupied orbital (Kohn−Sham) of **4a**.

significantly more powerful ligand than its phenyl analogue **3b**. Due to their high sensitivity to oxidation, these phosphole isomers were only characterized by ^{1}H, ^{13}C, and ^{31}P NMR.[7] In order to confirm their high nucleophilicity, they were complexed with $[W(CO)_5]$. It is known that the $^{1}J_{P-W}$ coupling constant is directly correlated with the electron-donating power of the P substituents: the higher the donation, the lower the coupling.[8] In our case, the $^{1}J_{P-W}$ coupling in the tungsten complex of **4c** is 227.8 Hz vs 228.5 Hz for the tBu_3P complex and 245 Hz for the Ph_3P complex. Both **4b** and **4c** were reacted with $PdCl_2$. Once again, their behaviors are different (eq 4).



All of these complexes were isolated and fully characterized, including X-ray crystal structure analyses. We give the data for **6** in Figure 2.

Since the energy levels of the lone pairs of **4c** and tris-*tert*-butylphosphine are identical at the same level of theory, we were led to check the catalytic properties of the palladium complexes of **4c** in the Suzuki cross-coupling of aryl chlorides with arylboronic acids. Tris-*tert*-butylphosphine and, more generally, bulky trialkylphosphine Pd complexes are known to be exceptionally efficient as catalysts for the Heck and Suzuki reactions.[9,10] Using the conditions described in the literature,[10] we found that complex **7** indeed catalyzes the

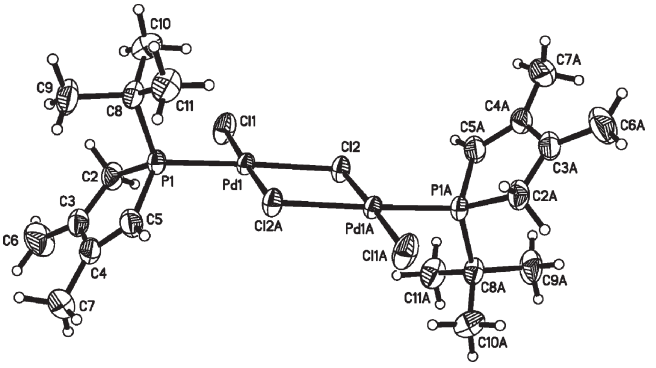
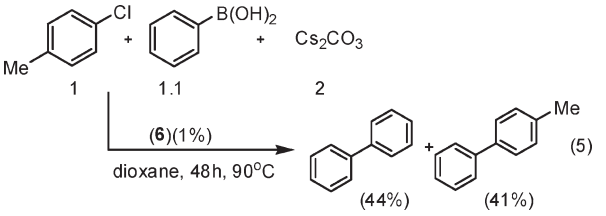
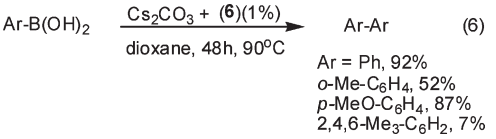


Figure 2. X-ray crystal structure of the dimeric complex **6**. Main bond lengths (Å) and angles (deg): P1−Pd1 = 2.2094(5), Pd1−Cl1 = 2.2775(6), Pd1−Cl2 = 2.4491(5), Pd1−Cl2A = 2.3277(5), C2−C3 = 1.445(4), C2−P1 = 1.808(2), C3−C6 = 1.396(3), C3−C4 = 1.459(4), C4−C5 = 1.400(3), C5−P1 = 1.800(2), C8−P1 = 1.854(2); C5−P1−C2 = 93.54(12).

cross-coupling of *p*-chlorotoluene with phenylboronic acid (eq 5).



The surprising result was that we got a great deal of biphenyl produced by deboronation homocoupling. This side reaction is known,[11] but its extent is exceptionally high. Thus, we were led to investigate more closely this transformation. The results are shown in eq 6.



It is clear that **6** deserves further investigation as a catalyst for homocoupling and that other uses of **4c** as a ligand for catalytic reactions are possible.

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Supporting Information Available: Text giving additional spectral data and CIF files giving details of the X-ray crystal structure analysis of compounds **5a**,**b** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

(7) **4b**: ^{31}P NMR δ −16 ppm; ^{1}H NMR ($CDCl_3$) δ 2.03 (s, Me), 2.65 (m, 1H, CH_2P), 3.10 (m, 1H, CH_2P), 5.05 (s br, 1H, =CH_2), 5.12 (s br, 1H, =CH_2), 6.24 (d, J_{HP} = 38.5 Hz, =CHP), 7.32 (m, 3H, *m*,*p*-Ph), 7.45 (m, 2H, *o*-Ph); ^{13}C NMR ($CDCl_3$) δ 16.71 (Me), 33.82 (d, J_{CP} = 7.6 Hz, CH_2P), 107.81 (d, J_{CP} = 3.8 Hz, =CH_2), 128.45 (d, J_{CP} = 7.6 Hz, CH(Ph)), 129.09 (s, *p*-CH(Ph)), 132.53 (d, J_{CP} = 20.0 Hz, CH(Ph)), 133.66 (d, J_{CP} = 13.3 Hz, =CHP), 140.61 (d, J_{CP} = 22.9 Hz, *ipso*-C(Ph)), 150.40 (s, β-C=), 152.55 (s, β-C=). **4c**: ^{31}P NMR δ 7.

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