Carbene Complexes

A Bis(thiophosphinoyl)methanediide Palladium Complex: Coordinated Dianion or Nucleophilic Carbene Complex?**

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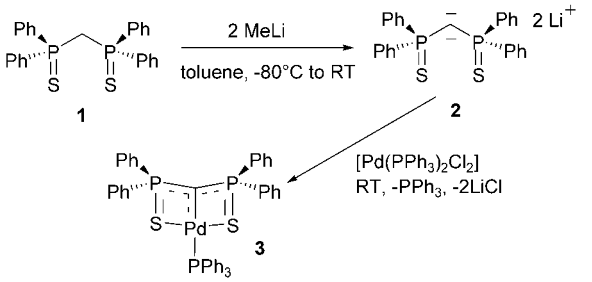
Transition-metal carbene complexes are one of the most widely studied organometallic species because of their high activity in numerous catalytic processes.[1] Most efforts were recently focused on the synthesis of isolable free carbene ligands.[2] However, new and rapid synthetic strategies allowing the generation of new carbenes in the coordination sphere of metals from easily available and cheap precursors have yet to be developed. In this perspective, phosphorus-substituted methane derivatives have attracted the attention of many groups as potential precursors.[3,4] Besides the particular electronic properties of phosphorus, which markedly differ from that of their nitrogen counterparts, the interest of such derivatives also resides in the possibility of using phosphorus as an anchor for other heteroatoms through oxidation of its lone pair. This approach was elegantly demonstrated by Cavell and co-workers who successfully developed the chemistry of bis(iminophosphorano)methanediide complexes.[5]

As part of a program aimed at exploring the use of thiophosphinoyl ligands in coordination chemistry and catalysis[6] we recently explored the possibility of generating analogous carbene complexes from the bis(diphenylthiophosphinoyl)methane ligand. This work was also motivated by the tendency of thiophosphinoyl ligands to favor coordination of electron-rich metal centers. Furthermore, sulfur ligands were rarely employed as ancillary ligands in carbene chemistry.[7] Herein, we report a new type of pincer ligand featuring a formal "carbenic" atom and two ancillary sulfide ligands.

The new dianion **2** was readily synthesized in quantitative yield through a double deprotonation of the methylene group in **1** using MeLi in toluene at low temperature (Scheme 1) following a similar procedure to that used for the deprotonation of bis(diphenyl-*N*-trimethylsilylphosphinimino)-methane.[8] Formation of **2** was evidenced by vigorous evolution of methane at room temperature and the formation, over two hours, of a yellow turbid mixture. Dianion **2** which is highly sensitive towards moisture gives rise to a singlet in the ^{31}P NMR spectrum at $\delta = 20.6$ ppm (121.5 MHz, toluene, 25 °C, 85 % H_3PO_4 as external standard) and was used without purification for further reactions. The reaction of **2** with $[(PPh_3)_2PdCl_2]$ yielded a burgundy red solution and a red precipitate. The ^{31}P NMR spectrum of the new species is highly diagnostic. Indeed the new complex **3** gives rise to an AX_2 spin system ($\delta(A) = 21.5$ ppm; $\delta(X_2) = +39.8$ ppm, CD_2Cl_2, 298 K) revealing a symmetrical structure featuring three phosphorus atoms (Scheme 1).



Scheme 1.

After work-up aimed at eliminating the LiCl salt formed and the free PPh_3 ligand, complex **3** was fully characterized by NMR spectroscopic techniques (^{1}H and ^{13}C) and elemental analyses. Though no ^{13}C NMR signal could be recorded for the carbenic carbon atom (as was reported by Cavell and co-workers for some carbene complexes[5g,h]), the absence of methylenic protons was confirmed by both ^{1}H and ^{13}C NMR spectroscopy. Fortunately, X-ray-quality red crystals of **3** were obtained either from a concentrated CH_2Cl_2 solution or by diffusion of hexanes into a CH_2Cl_2 solution of the complex (Figure 1).[9] Complex **3** was found to be remarkably resistant to moisture and it crystallizes with a molecule of CH_2Cl_2 a situation which already points towards a weak nucleophilic character. The shortest distances between the solvent and the C1 and Pd atoms are 5.0 and 5.9 Å, respectively.

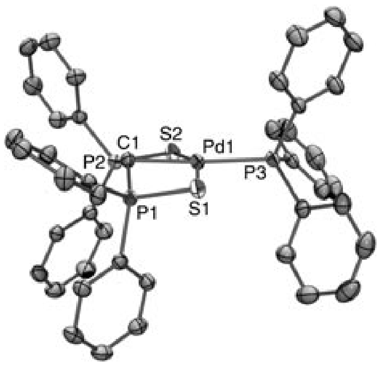


Figure 1. View of one molecule of **3** (thermal ellipsoids set at 50% probability). The hydrogen atoms and cocrystallized CH_2Cl_2 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1-C1 2.113(2), C1-P1 1.689(2), C1-P2 1.690(2), Pd1-S1 2.3741(6), Pd1-S2 2.3677(6), Pd1-P3 2.3030(6), P1-S1 2.0451(7), P2-S2 2.0424(8); P1-C1-P2 139.2(1), C1-Pd1-S1 80.63(6), S1-Pd1-P3 96.45(2), P3-Pd1-S2 103.78(2), S2-Pd1-C1 80.91(6), C1-Pd1-P3 174.61(6), S1-Pd1-S2 158.42(2).

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The structure of **3** definitely establishes the presence of a central tricoordinate carbon atom that is bound to the Pd center and the two PPh_2S groups. However, the relatively long C1–Pd separation (2.113(2) Å) rules out the formation of a true double bond (2.005 Å).[7] This bond is shorter than a classical single Pd–C bond (about 2.15 Å). Moreover, even though the overall geometry around the palladium center is square planar, the angle between the Pd–C1 bond and the plane defined by the "carbene moiety" measures 102.0°. Thus in **3**, the metal center seems to be located in a quasiperpendicular plane to the carbene fragment. Similar distortions, but to a lesser extent (angles varying between 0 and 37.7°), were also observed in some of Cavell's complexes.[5e] A striking feature is the very short P–C1 bonds of 1.689(2) and 1.690(2), which are similar to bond lengths found in carbodiphosphoranes and their complexes.[10] These short bonds very likely result from negative hyperconjugation from carbon to phosphorus σ^* orbitals. How can this geometry be rationalized? ONIOM calculations were carried out on the real system using the Gaussian 03 set of programs[11] (all phenyl groups were calculated at the MM level and the other atoms at the MQ level of theory).[12] Theoretical data are very similar to those given by X-ray crystallography with the exception of the P–S bond lengths which were found to be slightly longer.

The electronic structure of **3** can be rationalized by looking at the molecular orbital (MOs) which involve the n_p and n_σ nonbonding orbitals on the carbenic center.[13] Owing to the almost perpendicular orientation of the carbene ligand, the sigma bonding MO results from the interaction between the n_p orbital and a metal-centered orbital directed along the Pd–C axis. This doubly occupied MO characterizes a σ Pd–C bond since its antibonding counterpart (the LUMO of the complex) is vacant (Figure 2, right). The n_σ orbital interacts with the d_{xz} orbital through a π-type overlap. Note that both the bonding and the antibonding combinations are occupied, the latter being the HOMO of the complex (Figure 2, left). Therefore the π interaction does not lead to any π bonding character between the Pd and C1 centers. The bonding picture which emerges from this six-electron four-orbital analysis is that there is: 1) a single (σ) metal–carbon bond involving the n_p orbital on the carbenic center and 2) two nonbonding electron pairs on Pd and C1, the electron pair on the carbenic center is located approximately in the plane of the carbene (n_σ orbital). A way to understand this particular electronic structure is to consider that the complex results from the interaction between a $d^{10}PdL_3$ fragment and a neutral carbene (Figure 3): an occupied MO of the metal fragment interacts with the vacant n_p orbital, leading to a nearly perpendicular orientation of the carbene ligand (distorted "open book" conformation).[5e] A four-electron interaction develops between the n_σ and d_{xz} orbitals.

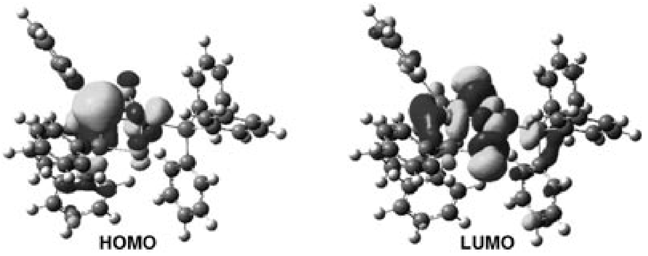


Figure 2. HOMO and LUMO of the theoretical structure of **3** as given by DFT calculations.

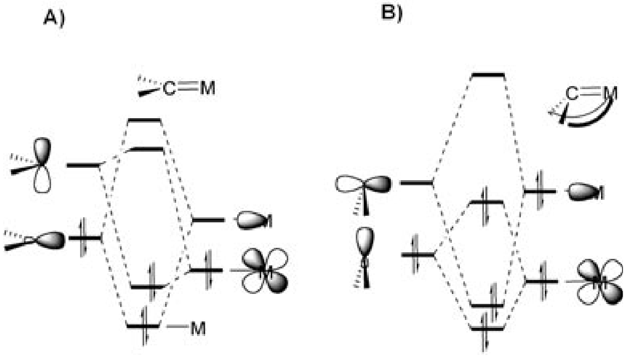


Figure 3. A) Usual bonding mode in carbene complexes, B) electronic situation in **3** assuming a $d^{10}PdL_3$ fragment.

Or, one can assume the two electrons of the σ bond to be associated to the carbenic ligand as is usual for electron counting in transition-metal complexes. Then, the whole complex can be described as a d^8 $[PdL_3]^{2+}$ metal fragment interacting with a dianionic carbenic center. A further interpretation is found by using the isolobal analogy. The T-shape $d^{10}PdL_3$ fragment is isolobal to CH_3^-, so that complex **3** is analogous to the $CH_3–CH_2^-$ ion (Figure 4) with a single C–C bond and a lone pair on the pyramidalized methylene moiety.[14]

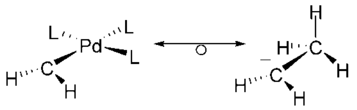
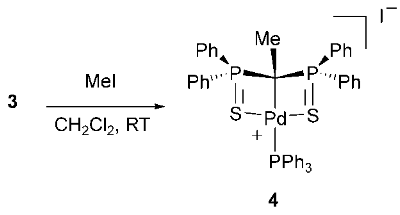


Figure 4. By the isolobal analogy complex **3** is analogous to the $CH_3–CH_2^-$ ion.

The nucleophilic character of the carbenic atom was confirmed by NBO calculations ($q_C = -1.39$ and $q_{Pd} = +0.37$). To demonstrate the presence of a reactive lone pair on this "carbenic" carbon atom, complex **3** was treated with various electrophiles. For example, the reaction with MeI, which was carried out in CH_2Cl_2 at room temperature, exclusively takes place on the carbon atom. The cationic complex **4** formed was isolated in a quantitative yield (Scheme 2).[15]

This new complex was fully characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. Orange crystals of **4** were grown by a slow diffusion of hexanes into a dichloromethane solution of the complex (see Supporting Information).[9] Interestingly, we note that the C–Pd bond in **4** (2.146(2) Å) is only slightly elongated with regard to **3** thus confirming the pronounced single-bond character of the C–Pd bond in **3** (2.113(2) Å). Theoretical



Scheme 2.

calculations using the ONIOM method (same level of theory than in **3**) yielded a structure which is very close to that experimentally observed. NBO calculations indicate that the palladium-bound carbon atom still bears a substantial negative charge ($q_C = -1.02$ and $q_{Pd} = +0.36$).

In conclusion, we have developed an easy synthetic access to a new type of nucleophilic "carbene" complex featuring two pendant thiophosphinoyl ancillary ligands. Theoretical calculations indicate that these new species can be either regarded as a coordinated dianion with a strong delocalization of the charge onto the two P–C bonds, or as a nucleophilic carbene complex.

Experimental Section

All experiments were carried out under dry argon or nitrogen atmosphere using distilled and degassed solvents.

3: Two equivalents of MeLi (0.84 mL, 1.6 M in diethyl ether, 1.34 mmol) were added to a solution of **1** (300 mg, 0.67 mmol) in toluene (5 mL) at −78 °C. The mixture was warmed to room temperature and stirred for 2 h leading to the formation of a yellow suspension of **2**. Then [$PdCl_2(PPh_3)_2$] (470 mg, 0.67 mmol) was added in one portion at room temperature. The resulting mixture immediately turned red and ^{31}P NMR spectroscopy showed the reaction to be complete by indicating the presence of complex **3** and PPh_3. Complex **3** and LiCl are poorly soluble in toluene and were isolated by centrifugation. Pure complex **3** was finally obtained in 88% yield (480 mg, 0.59 mmol) after dissolution in CH_2Cl_2 (6 mL) followed by filtration to remove LiCl and evaporation of the solvent. Selected data: ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 7.13$–7.66 ppm (m, 35H; H of phenyl); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25 °C, 85% H_3PO_4 as external standard): $\delta = 21.5$ (t, ^3J(P,P) = 14.6 Hz; PPh_3), 39.8 ppm (d, ^3J(P,P) = 14.6 Hz; PPh_2S); ^{13}C{^{1}H} NMR (75.465 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2 $\delta = 53.73$ ppm as internal reference): $\delta = 125.4$–139.1 ppm (m; C of phenyl), C-Pd not observed; elemental analysis (%) calcd for $C_{43}H_{35}P_3PdS_2$: C 63.35, H 4.33, found: C 62.97, H 4.05.

4: Complex **4** was obtained by adding MeI (27 μL, 0.43 mmol) to a solution of **3** (350 mg, 0.43 mmol) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred for five minutes and then taken to dryness. Complex **4** was thus isolated in a quantitative yield (100%, 410 mg, 0.43 mmol). Selected data: ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 1.86$ (dt, ^3J(H,P) = 16.2 Hz, ^4J(H,P) = 8.6 Hz, 3H; CH_3), 7.00–8.04 ppm (m, 35H; H of phenyl); ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25 °C, 85% H_3PO_4 as external standard): $\delta = 22.8$ (t, ^3J(P,P) = 15.8 Hz; PPh_3), 62.3 ppm (d, ^3J(P,P) = 15.8 Hz; PPh_2S); ^{13}C{^{1}H} NMR (75.465 MHz, CD_2Cl_2, 25 °C, CD_2Cl_2 $\delta = 53.73$ ppm as internal reference): $\delta = 20.7$ (pq, J(C,P) = 5.0 Hz; CH_3), 125.6 (dt, ^1J(C,P) = 48.0 Hz, ^2J(C,P) = 8.7 Hz; C-Pd), 127.7–135.4 ppm (m; C of phenyl); elemental analysis (%) calcd for $C_{44}H_{38}IP_3PdS_2$: C 55.21, H 4.00; found: C 55.10, H 3.87.

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[9] Crystal data for **3** ($C_{43}H_{35}P_3PdS_2\cdot\frac{1}{2}(CH_2Cl_2)$): space group $P2_1/c$, $a = 9.0270(10)$, $b = 36.1930(10)$, $c = 12.7440(10)$ Å, $\beta = 109.3620(10)°$, $V = 3928.2(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.450$ g cm^{-3}, $F(000) = 1748$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 0.800$ cm^{-1}; crystal dimensions 0.20 × 0.10 × 0.08 mm. Data collection was performed on a Nonius KappaCCD single crystal diffractometer at $T = 150$ K. Crystal structure was solved with SIR97,[16] refinement against F^2 (SHELXL97[17]) with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters. *hkl* ranges: −6 12; −46 50; −17 17, 22119 reflections collected, 11087 unique ($R_{int} = 0.0445$), 8922 data with $I > 2\sigma(I)$, 444 parameters refined, GOF(F^2) = 1.013, final R indices ($R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma\ w(F_o^2)^2]^{1/2}$, $R1 = 0.0403$, $wR2 = 0.1161$, max/min residual electron density 0.973(0.097)/−1.215(0.097) e Å^3. Crystal data for **4** are given in the Supporting Information. CCDC-245083 (**3**) and CCDC-245084 (**4**) contains the supplementary crystallographic data for this paper. These data can be

obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[13] Molecular orbitals of **3** were calculated at the MQ (B3PW91) level on the ONIOM structure using the 6-311+G** basis set for the carbenic atom, S, and P atoms and the 6-31G* for all phenyl groups (C and H atoms). Natural bond order (NBO) calculations were performed at the same level of theory for **3**.[22] For the theoretical structure of **4**, the 6-31+G* basis set was used for calculating the H atoms of the methyl group.

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