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Stable (Aryl)(phosphino)carbenes: New Ligands for Transition Metals

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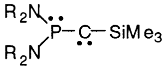
Over the years, the success of homogeneous catalysis can largely be attributed to the development of a diverse range of ligand frameworks that have been used to tune the behavior of the various systems. This has led to not only highly active and selective catalysts, but also to the discovery of fundamentally new types of transition metal-mediated transformations through a judicious choice of metal and ligand. A particularly good example is the recent spectacular achievements that have been made using N-heterocyclic carbene (NHC) ligands.[1] It is noteworthy that although NHC-transition metal complexes have been known since 1968[2] and that their organometallic chemistry was investigated by Lappert in the 1960's,[3] the recent developments in their application as scaffolds in catalysis have only been made possible because of the availability of *stable* N-heterocyclic carbenes.[4]



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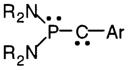

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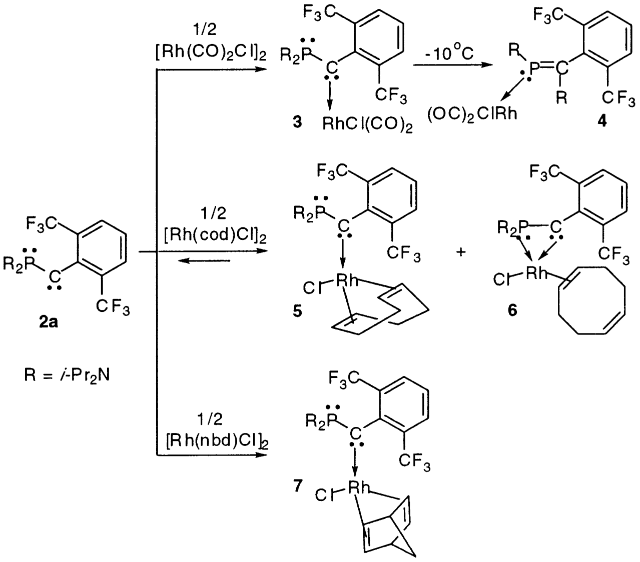
Despite the chronologically earlier discovery of stable (phosphino)(silyl)carbenes **1**,[5] direct complexation of these species has not yet been reported,[6−8] and only a few phosphinocarbene complexes are known.[9] The reluctance of carbenes **1** to act as ligands has recently been rationalized theoretically.[10] Our recent discovery that (phosphino)(aryl)carbenes **2** can also be isolated[11] prompted us to investigate their behavior as ligands. Notably, because the singlet−triplet separation is fairly small for phosphinocarbenes,[12] one would expect that the nature of the metallic fragment should play a crucial role in determining whether such η^1-carbene complexes adopt a Fischer- or a Schrock-type coordination mode. Furthermore, phosphinocarbenes could potentially act as four-electron donors (side-on complexation). This may be important if they were used as ligands during catalysis, as they may very well stabilize the coordinatively and electronically unsaturated "resting state" of the catalyst.[9b−e] In other words, the structural versatility, which is a great strength of NHC ligands, could be expanded further using the related phosphinocarbenes.

Here we report the direct synthesis of transition metal complexes from the stable phosphinocarbene **2a**. Both η^1- and η^2-coordination modes have been observed. A discussion of the nature of the carbene−metal bond is presented on the basis of spectroscopic data and of a single-crystal X-ray diffraction study.

Scheme 1



Treatment of the [bis(diisopropylamino)phosphino][2,6-bis(trifluoromethyl)phenyl]carbene **2a**[11] with one-half of an equivalent of $[RhCl(CO)_2]_2$ in toluene at −50 °C immediately and quantitatively affords the corresponding carbene complex **3** (Scheme 1). The ^{31}P NMR chemical shift of **3** (δ +109 ppm) is deshielded by 131 ppm as compared to that of the free carbene, and it now appears in the region typically associated with methylene phosphonium salts.[13] Moreover, the ^{13}C NMR chemical shift for the carbene center (δ 114.4 ppm, $^1J_{C-P} = 112$ Hz, $^1J_{C-Rh} = 29$ Hz) is shielded as compared to that of the free carbene (δ 146.1 ppm, $^1J_{C-P} = 271$ Hz), with two signals being observed for the CO ligands (δ 185.1 ppm, $^1J_{C-Rh} = 75$ Hz and δ 186.1 ppm, $^1J_{C-Rh} = 58$ Hz, $^3J_{P-C} = 5$ Hz). All of these data are similar to those observed for the corresponding N-heterocyclic carbene complex[14] and suggest a Fischer-type structure. However, compound **3** could not be structurally characterized because it quickly isomerizes at −10 °C. The migration of both an amino group (from phosphorus to carbon) and the metallic fragment (from carbon to phosphorus) leads to the corresponding η^1-phosphaalkene complex **4**.

Subsequently, the reaction of **2a** with one-half of an equivalent of $[RhCl(cod)]_2$ in toluene at room temperature was investigated (Scheme 1). Because of the enhanced steric hindrance from the cod ligand, the coordination of the carbene moiety is much less favored than with $[RhCl(CO)_2]_2$. As a result, an equilibrium is established with three components being detectable by ^{31}P NMR spectroscopy in an approximate ratio of **2a**/**5**/**6**: 16/1/2. The η^1-coordination mode proposed for carbene complex **5** is supported by the similarity between the ^{31}P NMR chemical shifts of **5** (δ 109.7 ppm) and **3**. In contrast, complex **6** adopts an η^2-coordination

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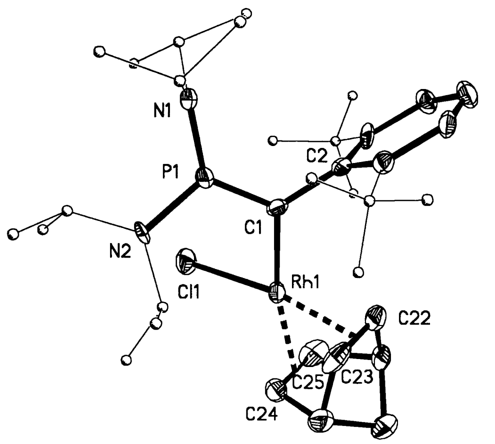

Figure 1. Thermal ellipsoid diagram (50% probability) of **7**. For clarity, the *i*-Pr and CF_3 groups have been simplified. Selected bond lengths (Å) and angles (deg): C1−Rh1 2.096(7), P1−C1 1.673(7), C1−C2 1.513(9), Rh1−Cl1 2.397(2), Rh1−C22 2.104(7), Rh1−C23 2.111(8), Rh1−C24 2.183(7), Rh1−C25 2.178(7), P1−C1−C2 119.0(5), P1−C1−Rh1 121.4(4), C2−C1−Rh1 119.5(4), N1−P1−C1 128.0(3), N2−P1−C1 119.0(3), N1−P1−N2 111.2(3).

mode as deduced from the shielding of the ^{31}P NMR signal (δ ^{31}P −28.9 ppm, $^1J_{P-Rh} = 138$ Hz). Moreover, the ^{13}C NMR chemical shift for the carbene center (δ 212.4 ppm, $^1J_{C-P} = 31$ Hz, $^1J_{C-Rh} = 36$ Hz) is significantly deshielded as compared to that of the free carbene, appearing in the range characteristic of η^2-phosphinocarbene complexes acting as four-electron donors.[9b−e] However, the small quantity of both carbene complexes **5** and **6** present in the reaction mixture yet again precluded any attempts at crystallization and structural analysis.

Because the equilibrium could not be displaced using a nonchelating ligand such as cyclooctene (coe),[15] the reaction of **2a** with one-half of an equivalent of the somewhat less sterically demanding $[RhCl(nbd)]_2$ was carried out (Scheme 1). The carbene complex **7** was instantaneously and quantitatively obtained. The spectroscopic data (δ ^{31}P 100.8 ppm, δ ^{13}C 120.6 ppm, $^1J_{C-P} = 2$ Hz, $^1J_{C-Rh} = 59$ Hz) are very similar to those for **3** and **5**, supporting an η^1-coordination mode. Pale yellow crystals of **7** (mp: 156 °C dec) suitable for an X-ray diffraction study were obtained by cooling a dichloromethane/pentane solution to −80 °C. The molecular structure of **7** is shown in Figure 1 along with the pertinent metric parameters.[16] The carbene center adopts a trigonal planar environment with the plane defined by P1−C1−C2 being twisted by about 47° out of the square coordination plane around the rhodium. As predicted by Schoeller et al.,[10] coordination induces a considerable contraction of the carbene bond angle (from 162° in the free carbene to 119° in **7**). The carbene−rhodium bond distance [2.096(7) Å] is in the range typical for C−Rh single bonds, but is slightly longer than that observed for related N-heterocyclic carbene rhodium complexes (2.00−2.04 Å). These data suggest that **7** is best regarded as a Fischer-type carbene complex. In other words, the carbene−metal interaction results from the donation of the carbene lone pair into an empty metal-based orbital. Back-donation from the metal to the carbene center is almost negligible as compared to that from the phosphorus lone pair. The phosphorus atom adopts a trigonal planar geometry with a PC bond distance of 1.673(7) Å, which is longer than that in the free carbene, 1.544(3) Å, but is still short. Note that, in this case, the inherent chelation of the nbd ligand prevents the formation of an η^2-complex analogous to **6**.

Given the broad range of stable or persistent aryl- or even alkyl-(phosphino)carbenes now available,[11,17] their direct coordination to transition metal fragments opens the way for the preparation of a variety of new carbene complexes. Further examination of the various coordination modes and of the ensuing carbene−metal interactions is currently in progress to define the potential use of these carbene complexes in homogeneous catalysis.

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Supporting Information Available: Selected spectroscopic data for **3**−**7** (PDF) and X-ray crystallographic data for **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal data for **7**: $C_{35}H_{47}ClF_6N_2PRh$, $M = 779.08$, monoclinic, space group $P2_1/n$, $a = 10.355(2)$, $b = 13.057(2)$, $c = 26.794(4)$ Å, $\beta = 90.973(3)°$, $V = 3622.1(9)$ Å^3, $Z = 4$, $T = 173(2)$ K, crystal size 0.05 × 0.3 × 0.7 mm^3, $1.52° \leq \theta \leq 22.46°$, 14 590 reflections (4699 independent, R int = 0.0932), $T_{min}/T_{max} = 0.500027$, 452 parameters, R1 [$I > 2\sigma(I)$] = 0.0611, wR2 [all data] = 0.1328, largest electron density residue: 1.134 e Å^{-3}. Data were collected using an oil-coated shock-cooled crystal on a Brucker-AXS CCD 1000 diffractometer ($\lambda = 0.71073$ Å, Mo Kα). Semiempirical absorption corrections were employed.[18] The structure was solved by direct methods (SHELXS-97)[19] and refined using the least-squares method on F^2.[20] Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-193095 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk].
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