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α, β-(Phosphino)(aminocarbene) and α, ω-(phosphino)(oxyaminocarbene): new bidentate ligands for transition metal complexes

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Abstract

Direct complexation of (amino)(phosphino)carbene **1a** and (amino)(oxy)carbene **1b** featuring a phosphino group in position-6 to the carbene with $[Rh(CO)_2Cl]_2$ has been studied. With the 1,2-bidentate ligand **1a**, an original cationic complex **2** featuring two (amino)(phosphino)carbenes η^2-bonded to the metal has been isolated in 79% yield. In the case of the 1,6-bidentate ligand **1b**, a rhodium(I) complex **3** in which the carbene is in *trans* position relative to the CO ligand was obtained in 85% yield. Both compounds were fully characterized including X-ray diffraction studies.

Keywords: (Amino)(phosphino)carbene; (Amino)(oxy)carbene; Bidentate ligands; Rhodium complexes

1. Introduction

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 behaviour of the various systems. 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 sixties [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]. Although it is possible to tune the structure of carbene ligands to some extent, the diversity possible is by far out reached by that possible for their phosphorus-based counterparts. Obstacles to extending the range of carbenes available mainly reside in the supposed inherent instability of carbenes, which is explained by their six-valence-electron shell that defies the octet rule. Our group has prepared a variety of new types of stable carbene. However, direct complexation of the first of them, namely the (phosphino)(silyl)carbenes [1a,5], has not yet been reported, and all our attempts have failed. The apparent reluctance of these carbenes to act as ligands has recently been tentatively rationalized by theoretical studies [6]. In marked contrast, we have found that treatment of the [2,6-bis(trifluoromethyl)phenyl](phosphino)carbene **A** [7] with half an equivalent of $[RhCl(nbd)]_2$ in toluene at −50 °C immediately and quantitatively affords the corresponding carbene complex **B** (Scheme 1) [8]. Based on NMR spectroscopy and X-ray diffraction study, we concluded that the carbene–metal interaction consists almost exclusively of donation of the carbene lone pair into an empty metal-based orbital. Back-donation from the metal to the carbene center is negligible compared to that from the phosphorus lone pair. Carbene **A** is a strong σ-donor!

Here we report the direct synthesis of transition metal complexes from the stable (amino)(phosphino)carbene

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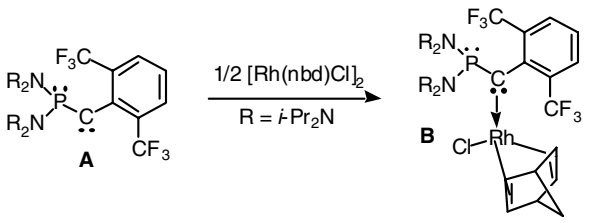
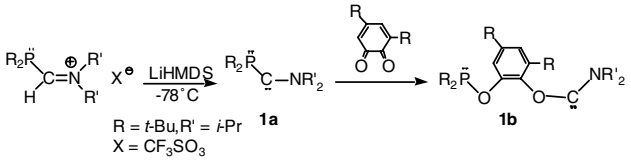


Scheme 1.



Scheme 2.

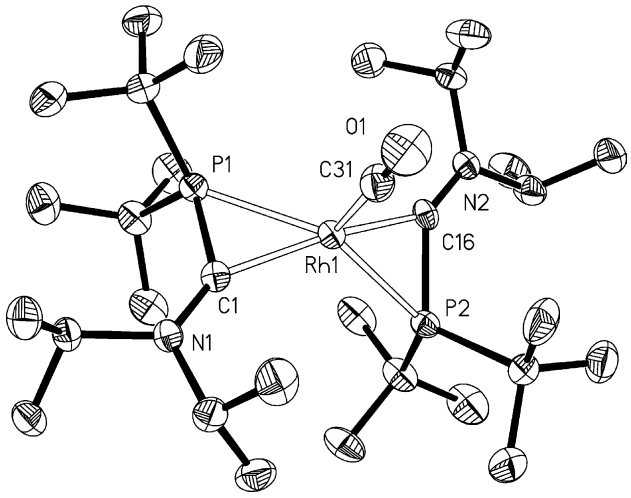


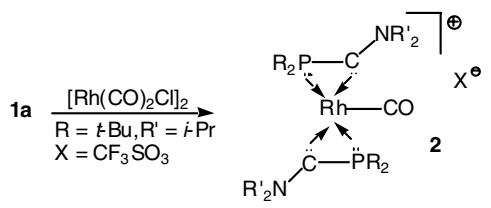
Fig. 1. Solid state structure of complex **2** (ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh(1)–C(1) 2.000(3); Rh(1)–C(16) 2.007(3); Rh(1)–C(31) 1.891(3); Rh(1)–P(1) 2.3480(8); Rh(1)–P(2) 2.3262(8); C(1)–N(1) 1.299(4); C(16)–N(2) 1.302(4); P(1)–C(1) 1.791(3); P(2)–C(16) 1.798(3); C(31)–O(1) 1.135(4); P(1)–Rh(1)–C(1) 47.83(9); P(2)–Rh(1)–C(16) 48.36(9); P(1)–Rh(1)–C(31) 110.04(10); C(1)–Rh(1)–C(31) 99.57(13); P(2)–Rh(1)–C(31) 112.05(10); C(16)–Rh(1)–C(31) 100.35(13).

1a [9] and (amino)(oxy)carbene **1b** [10] featuring a phosphino group in position-6 with respect to the carbene center. Carbene **1a** has been prepared by deprotonation of the corresponding iminium salt, while carbene **1b** has been synthesized by simple addition of the 3,5-di-*tert*-butyl-*ortho*-quinone to carbene **1a** (Scheme 2).

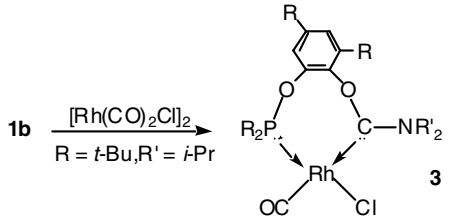
2. Results and discussion

The (phosphino)(amino)carbene **1a** reacted at −78 °C with 0.25 equivalent of $[Rh(CO)_2Cl]_2$. The reaction proceeded very cleanly, and complex **2** was isolated as red crystals in 79% yield by recrystallization from a THF solution at −30 °C (Scheme 3). The presence of two phosphinocarbene ligands was indicated by the multiplicity of the ^{13}C NMR signals for the CO (201.0, dt, $J_{Rh-C} = 86$, $J_{P-C} = 16$ Hz) and $C_{carbene}$ nuclei (227.0, dt, $J_{Rh-C} = 24$, $J_{P-C} = 24$ Hz). The high field position (−58.6 ppm) and the large phosphorus–rhodium coupling constant ($J_{P-Rh} = 102$ Hz) observed in the ^{31}P NMR spectrum suggested the formation of three-membered metallocycles. The η^2-coordination mode was unambiguously established by an X-ray diffraction study (Fig. 1). Complex **2** adopts a distorded square-based pyramid structure with the CO ligand in axial position. The carbene–rhodium bond distances (2.00 Å) are in the range typical for C–Rh single bonds, and very similar to that observed for related *N*-heterocyclic carbene rhodium complexes (2.00–2.04 Å) [11]. The phosphorus–rhodium bond distance (2.348 Å) lies at the upper limit of the range typical for P–Rh single bonds [12]. The nitrogen atom adopts a trigonal planar geometry with a short NC bond distance of 1.30 Å, which is identical to that of free (amino)(phosphino)carbenes (1.30 Å). This indicates that, 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 centre is almost negligible compared to that from the nitrogen lone pair.

Rhodium complex **3** was prepared by treatment of a THF solution of the (amino)(oxy)carbene **1b** with 0.5 equivalent of $[Rh(CO)_2Cl]_2$. It was isolated in 85% yield as yellow crystals by slow recrystallisation from a pentane solution at 0 °C (Scheme 4). The ^{31}P NMR spectrum showed a sharp doublet at 202 ppm with a large phosphorus–rhodium coupling constant (199 Hz) and in



Scheme 3.



Scheme 4.

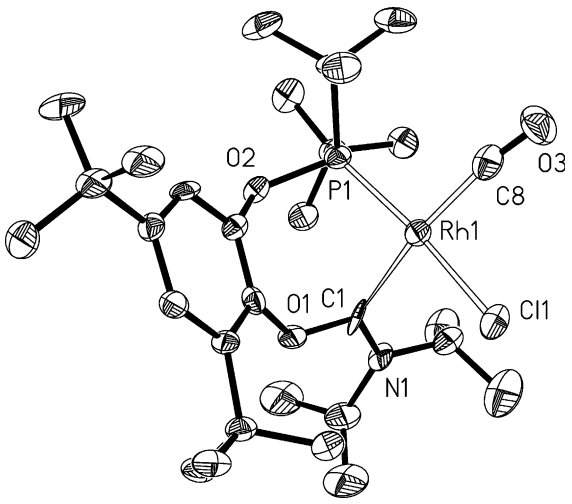


Fig. 2. Solid state structure of complex **3** (ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh(1)–C(1) 2.079(9); Rh(1)–P(1) 2.225(2); Rh(1)–C(8) 1.870(10); Rh(1)–Cl(1) 2.396(2); C(1)–N(1) 1.324(11); C(1)–O(1) 1.330(9); C(8)–O(3) 1.148(10); P(1)–Rh(1)–C(1) 90.0(2); C(1)–Rh(1)–Cl(1) 88.3(2); P(1)–Rh(1)–C(8) 97.0(3); C(8)–Rh(1)–Cl(1) 85.8(3).

the ^{13}C NMR spectrum the $C_{carbene}$ nuclei appeared to be also coupled to ^{103}Rh ($\delta = 226$ ppm, $J_{Rh-C} = 47$ Hz), which suggest that both the phosphine and carbene fragments are coordinated to the metal. Interestingly only one isomer is formed and the *trans*-orientation of the carbene with respect to the CO ligand has been established by a single crystal X-ray diffraction study (Fig. 2). The rhodium center is in a nearly square planar environment (sum of bond angles around Rh 361.1°). The Rh–P distance of 2.225 Å is slightly shorter compare with the expected value for a rhodium(I)–phosphine complex [12]. Interestingly, the Rh–$C_{carbene}$ bond length of 2.079 Å is very similar to the values observed in rhodium complexes bearing a Cl and a diaminocarbene ligand *cis* to one another [13]. These observations are in line with the observed frequency of the IR absorption ν(CO) (1997 cm^{-1}) [14].

3. Conclusion

The (amino)(phosphino)carbene **1a** and (amino)(oxo) carbene **1b** are certainly excellent candidates as ligand for transition metal catalysts, in which a strong σ-donor ligand and a relatively labile ligand are desirable.

4. Experimental

All experiments were carried out under dry argon using standard Schlenk or dry box techniques. THF was distilled under argon from sodium benzophenone. ^{31}P NMR, ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX400 instrument. Chemical shifts are reported in ppm downfield from Me_4Si and were referenced to solvent peaks (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P). Coupling constants are given in Hz. $[Rh(CO)_2Cl]_2$ was used as supplied from Aldrich.

4.1. Synthesis of the (amino)(phosphino)carbene *1a*

To a THF solution (5 ml) of C-(phosphino)iminium salt (0.2 mmol) was added 1.5 equivalent of LiHMDS at −60 °C. Immediately a red colour appeared, and the ^{31}P NMR spectroscopy indicated the quantitative formation of carbene **1a**. This compound can be stored in solution for a few days at 0 °C, and was used without any further purification. ^{31}P-NMR (THF-d_8): 7.9 ppm. ^{1}H-NMR (THF-d_8): 1.11 (d, 18H, $^{3}J_{P-H} = 10.8$, CH_3CP), 1.30 (d, 12H, $^{3}J_{H-H} = 6.4$, CH_3CN), 4.50 (m, 1H, CHN), 5.31 (m, 1H, CHN). ^{13}C-NMR (THF-d_8): 20.5 (m, CH_3CHN), 24.7 (m, CH_3CHN), 29.4 (d,$^{2}J_{P-C} = 13.9$, CH_3C), 32.6 (d,$^{1}J_{P-C} = 18.9$, CH_3CP), 52.9 (m, CHN), 63.3 (m, CHN), 346.6 (d, $^{1}J_{P-C} = 57.3$, PCN).

4.2. Synthesis of the (amino)(oxo)carbene *1b*

To a THF solution (5 ml) of (amino)(phosphino)carbene **1a** (0.2 mmol) was added 1 equivalent of 3,5-di-*tert*-butyl-*ortho*-quinone at −30 °C. Immediately a deep green colour appeared, and the ^{31}P NMR spectroscopy indicated the quantitative formation of carbene **1b**. After evaporation of the solvent, carbene **1b** was obtained as a deep green oil (90% yield). ^{31}P-NMR (THF-d_8, 253 K):152.5. ^{1}H-NMR (THF-d_8, 253 K):1.17 (d, 18H, $J_{P-H} = 11.2$, CH_3CP), 1.26 (d, 6H, $J_{H-H} = 6.6$, CH_3CN), 1.33 (s, 9H, CH_3C), 1.37 (s, 9H, CH_3C), 1.42 (d, 6H, $J_{H-H} = 6.3$, CH_3CN), 3.85 (sept, 1H, $J_{H-H} = 6.3$, CHN), 5.21 (sept, 1H, $J_{H-H} = 6.6$, CHN), 6.97 (d, 1H, $J_{H-H} = 1.52$, H_{aro}), 7.44 (dd, 1H, $J_{H-H} = 1.52$ Hz, $J_{P-H} = 2.8$, H_{aro}); ^{13}C-NMR (THF-d_8, 253 K): 20.2 (s broad, CH_3CHN), 26.0 (s broad, CH_3CHN), 27.4 (d, $J_{P-C} = 15.5$, CH_3CP), 30.5 (s, CH_3C), 31.4 (s, CH_3C), 34.9 (s, CH_3C), 35.3 (s, CH_3C), 35.8 (d, $J_{P-C} = 25.7$, CH_3CP), 43.2 (s, CHN), 46.8 (s, CHN), 113.9 (d, $J_{P-C} = 24.2$ Hz, C_{aro}), 115.4 (s, C_{aro}), 140.8 (s, C_{aro}), 145.8 (s, C_{aro}), 146.5 (s, C_{aro}), 152.2 (d, $J_{P-C} = 9.1$ Hz, C_{aro}), 268.1 (s, O–C–N).

4.3. Synthesis of the (amino)(phosphino)carbene rhodium complex *2*

A THF solution (5 ml) of (amino)(phosphino)carbene **1a** (0.2 mmol) was added to 0.25 equivalent of $[Rh(CO)_2Cl]_2$ at −78 °C. After the solution mixture was warmed to room temperature, ^{31}P NMR spectroscopy indicated the quantitative formation of complex **2**,

which was obtained as a red powder after evaporation the solvent. Red crystals of **2** were obtained from a THF solution at −30 °C (79% yield). m.p. 155–156 °C. ^{31}P-NMR (THF-d_8): −58.6 ppm (d, $J_{Rh-P} = 102$). ^{1}H-NMR (THF-d_8): 1.37 (m, 18H, CH_3CP), 1.46 (m, 18H, CH_3CP), 1.47 (d, $J_{H-H} = 6.2$, 6H, CH_3–CH), 1.55 (d, $J_{H-H} = 6.4$, 6H, CH_3–CH), 1.85 (d, $J_{H-H} = 6.4$, 6H, CH_3–CH), 1.97 (d, $J_{H-H} = 6.2$, 6H, CH_3–CH), 4.22 (sept, $J_{H-H} = 6.2$, 2H, C*H*–N), 4.63 (sept, $J_{H-H} = 6.4$, 2H, C*H*–N). ^{13}C-NMR (THF-d_8): 19.2 (s, CH_3–CH), 20.3 (s, CH_3–CH), 21.2 (s, CH_3–CH), 21.3 (s, CH_3–CH), 30.5 (s, CH_3–C), 31.8 (s, CH_3–C), 36.9 (s, CH_3CP), 37.1 (s, CH_3CP), 52.6 (s, *CH*N), 74.9 (s, *CH*N), 201.0 (dt, $J_{Rh-C} = 86$, $J_{P-C} = 16$, CO), 227.0 (dt, $J_{Rh-C} = 24$, $J_{P-C} = 24$, PC).

4.4. Synthesis of (amino)(oxo)carbene rhodium complex 3

A THF solution (5 ml) of amino(oxy)carbene **1b** (0.2 mmol) was added to 0.5 equivalent of $[Rh(CO)_2Cl]_2$ at −78 °C. After the solution mixture was warmed to room temperature, ^{31}P NMR spectroscopy indicated the quantitative formation of complex **3**. After evaporation the solvent, the residue was extracted with pentane (50 ml). Yellow crystals of **3** were obtained from a pentane solution at 0 °C (85% yield). m.p. 149 °C (dec.). ^{31}P-NMR ($CDCl_3$): 202 ppm (d, $J_{Rh-P} = 199$). ^{1}H-NMR ($CDCl_3$): 1.27 (s, 9H, CH_3C), 1.39 (s, 9H, CH_3C), 1.41 (d, $J_{P-H} = 16.0$, 18H, CH_3CP), 1.50 (d, $J_{H-H} = 6.6$, 6H, CH_3–CH), 1.60 (d, $J_{H-H} = 6.6$, 6H, CH_3–CH), 4.17 (m, 1H, C*H*–N), 6.50 (sept, $J_{H-H} = 6.6$, 1H, C*H*–N), 7.21 (m, 2H, H_{aro}). ^{13}C-NMR ($CDCl_3$): 24.5 (s broad, CH_3–CH), 27.0 (s broad, CH_3–CH), 29.7 (d, $J_{P-C} = 6$, CH_3–CP), 31.6 (s, CH_3–C), 31.8 (s, CH_3–C), 35.0 (s, CH_3C), 35.9 (s, CH_3C), 39.1 (dd, $J_{Rh-C} = 2$, $J_{P-C} = 22$, CH_3CP), 50.1 (s, *CH*N), 58.7 (s, *CH*N), 121.0 (s, C_{aro}), 121.0 (d, $J_{P-C} = 2$, C_{aro}), 143.0 (d, $J_{P-C} = 2$, C_{aro}), 143.1 (s, C_{aro}), 146.2 (d, $J_{P-C} = 7$, C_{aro}), 147.7 (s, C_{aro}), 193.9 (dd, $J_{Rh-C} = 57$, $J_{P-C} = 14$, CO), 226.2 (d, $J_{Rh-C} = 47$, RhCN). IR (CH_2Cl_2): 1997 cm^{-1} (CO).

4.5. Crystallographic data for complexes 2 and 3

Data for all structures were collected at low temperature $T = 173(2)$ K using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS 97) [15] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2 [16]. Crystal data for **2**: $C_{36}H_{72}F_3N_2O_5P_2RhS$, $M = 866.87$, monoclinic, space group $P2_1/n$ with $a = 19.3806(15)$, $b = 11.0293(9)$, $c = 20.6518(16)$ Å, $\beta = 93.259(2)$, $V = 4407.3(6)$ Å^3, $Z = 4$. 25,024 reflections (9039 independent, $R_{int} = 0.0487$), largest electron density residue: 0.980 e Å^{-3}, $R_1 = 0.044$ (for $I > 2\sigma(I)$) and $wR_2 = 0.0862$ (all data). Crystal data for **3**: $C_{30}H_{52}ClNO_3PRh$, $M = 644.06$, monoclinic, space group $P2_1/n$ with $a = 12.438(3)$, $b = 20.513(5)$, $c = 13.205(3)$ Å, $\beta = 103.907(4)°$, $V = 3270.4(12)$ Å^3, $Z = 4$. 12,500 reflections (3939 independent, $R_{int} = 0.1086$), largest electron density residue: 1.453 e Å^{-3}, $R_1 = 0.0587$ (for $I > 2\sigma(I)$) and $wR_2 = 0.1468$ (all data).

5. Supplementary material

CCDC-226835 [**2**], 226836 [**3**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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 e-mail: deposit@ccdc.cam.ac.uk).

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