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The First Coordination of an (α-Diazo)phosphine to a Transition-Metal Center

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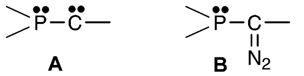
*Summary: Reaction of [o-(trifluoromethyl)phenyl][bis(diisopropylamino)phosphino]diazomethane (**1**) with tetracarbonylbis(μ-chloro)dirhodium(I) ($[Rh(CO)_2(\mu\text{-}Cl)]_2$) affords the monometallic complex **2** at low temperature and the dinuclear complex **3** upon warming to 0 °C. X-ray diffraction studies demonstrate that the coordination occurs via the phosphorus lone pair with retention of the diazo moiety in both complexes.*

Over the last 10 years, N-heterocyclic carbenes (NHCs) have become commonplace ligands, finding applications as scaffolds in a broad range of transition-metal-mediated transformations.[1] Despite the availability of NHCs as free, stable species,[2] many of the catalytically relevant metal complexes are prepared from masked forms (such as conjugated acids,[3] dimers,[4] alcohol adducts,[5] etc.).

In contrast, the coordination chemistry of the other family of stable carbenes, namely (phosphino)carbenes **A**, has been somewhat overlooked (Chart 1).[6−8] The first (phosphino)carbene complexes were prepared (in poor yields) either by coupling a metal-bound carbyne ligand with a phosphorus fragment or, alternatively, by C−H activation of PMe_3.[6] We have recently shown that direct complexation is also feasible,[9] both η^1- as well as η^2-rhodium(I) complexes being obtained from a stable (phosphino)(aryl)carbene.[10] Since all the (phosphino)carbenes are extremely moisture sensitive, we became interested in using their considerably more robust diazo precursors **B**[11] as potential synthons for the preparation of (phosphino)carbene complexes. Indeed, ever since the pioneering work of Yates,[12a] Werner,[12b−d] and Hermann,[12e−g] diazo compounds have routinely been used to prepare transition-metal carbene complexes. Here, we report that, surprisingly, (α-diazo)phosphines **B** coordinate[13] to rhodium(I) via the phosphorus lone pair, with retention of the diazo moiety. The resulting mono- and dinuclear complexes **2** and **3** are the first rhodium(I) *cis*-chloro dicarbonyl phosphine and dinuclear monosubstituted complexes, respectively, to be structurally characterized.

Chart 1. Structures of (Phosphino)carbenes A and (α-Diazo)phosphines B



The (α-diazo)phosphine **1**,[10c] featuring the *o*-(trifluoromethyl)phenyl substituent, and tetracarbonylbis(*μ*-chloro)dirhodium(I) were chosen because both fragments afford an interesting compromise between stability and reactivity. Irrespective of the temperature, addition of $^1/_2$ equiv of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ to **1** in diethyl ether led to a mixture of starting material **1** and the P-coordinated complex **2**, as deduced from the ^{31}P NMR chemical shift

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(1) (a) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181. (b) Herrmann, W. A.; Weskamp, T.; Bohm, V. P. W. *Adv. Organomet. Chem.* **2002**, *48*, 1. (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

(2) (a) Bourissou, D.; Guerret, O.; Gabbaï F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913.

(3) (a) Köcher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261. (b) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371. (c) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93.

(4) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185.

(5) (a) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953. (b) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem.* **2002**, *649*, 219.

(6) Bourissou, D.; Bertrand, G. *Adv. Organomet. Chem.* **1999**, *44*, 175.

(7) For attempted coordination of an anionic bis(phosphino)carbene, see: Fuchs, A.; Gudat, D.; Nieger, M.; Schmidt, O.; Sebastian, M.; Nyulaszi, L.; Niecke, E. *Chem. Eur. J.* **2002**, *8*, 2188.

(8) For theoretical investigations of (phosphino)carbene complexes, see: (a) Schoeller, W. W.; Eisner, D.; Grigoleit, S.; Rozhenko, A. J. B.; Alijah, A. *J. Am. Chem. Soc.* **2000**, *122*, 10115. (b) Schoeller, W. W.; Rozhenko, A. J. B.; Alijah, A. *J. Organomet. Chem.* **2001**, *617*, 435.

(9) Despagnet, E.; Miqueu, K.; Gornitzka, H.; Dyer, P. W.; Bourissou, D.; Bertrand G. *J. Am. Chem. Soc.* **2002**, *124*, 11834.

(10) (a) Buron, C.; Gornitzka, H.; Romanenko, V.; Bertrand, B. *Science* **2000**, *288*, 834. (b) Despagnet, E.; Gornitzka, H.; Rozhenko, A. B.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Angew. Chem.* **2002**, *114*, 2959; *Angew. Chem., Int. Ed.* **2002**, *41*, 2835. (c) Despagnet-Ayoub, E.; Solé, S.; Gornitzka, H.; Rozhenko, A. B.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *J. Am. Chem. Soc.* **2003**, *125*, 124.

(11) Baceiredo, A.; Bertrand, G.; Sicard, G. *J. Am. Chem. Soc.* **1985**, *107*, 4781.

(12) (a) Yates, P. *J. Am. Chem. Soc.* **1952**, *74*, 5376. (b) Werner, H.; Richards, J. H. *J. Am. Chem. Soc.* **1968**, *90*, 4976. (c) Wolf, J.; Brandt, L.; Fries, A.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 510. (d) Schwab, P.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1480. (e) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 599. (f) Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245. (g) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.

(13) End-on coordination of the terminal diazo nitrogen was postulated in the reaction of the lithium salt of the [bis(diisopropylamino)-phosphino]diazomethane with $Rh(PMe_3)_4Cl$: Menu, M. J.; Crocco, G.; Dartiguenave, M.; Dartiguenave, Y.; Bertrand, G. *Organometallics* **1988**, *7*, 2231.

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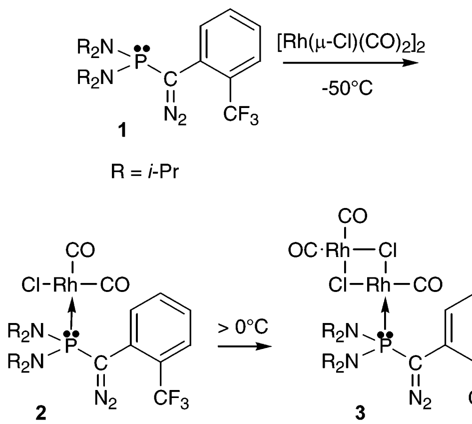
Scheme 1. Synthesis of Complexes 2 and 3



(118.1 ppm) and the magnitude of the J_{PRh} coupling constant (162 Hz). To achieve complete conversion of **1**, an excess of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ was required.[14] Complex **2** is indefinitely stable in solution at −50 °C but evolves over a period of a few hours at 0 °C to afford the new P-coordinated complex **3**, as a 4/1 mixture of the two NMR-distinguishable conformers **3a** and **3b** (^{31}P NMR 126.8 and 127.8 ppm) (Scheme 1). Complex **3** is also stable for days at −50 °C but decomposes within the space of a few hours at room temperature, leading to a complex mixture of products. No trace of the desired (phosphino)carbene complex could be detected. Complexes **2**[16] and **3**[17] were characterized at low temperature by multinuclear NMR spectroscopy[18] as well as through X-ray diffraction studies.[19]

The monometallic structure and cis geometry of **2** were suggested by the presence of two carbonyl resonances in the ^{13}C NMR spectrum that exhibit $^2J_{PC}$ coupling constants of 16 and 155 Hz, respectively.[20a] These structural features were confirmed by an X-ray analysis[19] performed on single crystals obtained from a saturated diethyl ether solution of **2** at −80 °C. The molecular structure of **2** is shown in Figure 1 along with the pertinent metric parameters.

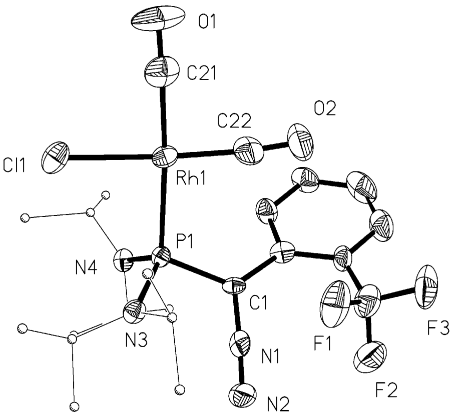


Figure 1. Molecular structure of **2** in the solid state. For clarity the hydrogen atoms are omitted and the isopropyl groups are simplified. Selected bond lengths (Å) and angles (deg): P1−C1 = 1.818(7), P1−Rh1 = 2.367(2), Rh1−C22 = 1.824(9), Rh1−C21 = 1.895(8), P1−N3 = 1.691(5), P1−N4 = 1.674(5), Rh1−Cl1 = 2.364(2), Rh1−C21 = 1.895(8), Rh1−C22 = 1.824(9); P1−C1−N1 = 115.8(4), P1−C1−C2 = 126.6(4), N1−C1−C2 = 117.2(5), C1−P1−N3 = 100.7(3), C1−P1−N4 = 105.8(3), C1−P1−Rh1 = 112.7(2), P1−Rh1−Cl1 = 90.46(7), P1−Rh1−C21 = 175.7(2), P1−Rh1−C22 = 95.6(2).

The rhodium center adopts a slightly distorted square planar geometry ($\Sigma_{angles} = 360.26°$), with the phosphorus−rhodium bond distance (2.367(2) Å) being at the longer end of the range typical for P−Rh single bonds.[21] A significant inequivalence of the Rh−C bond distances for the two carbonyl ligands (Rh−CO(cis to P) = 1.824(9) Å and Rh−CO(trans to P) = 1.895(8) Å) is observed, something that is consistent with the different trans influences of phosphine and chloride. Complex **2** is the first rhodium(I) *cis*-chloro dicarbonyl phosphine complex to be structurally characterized. Until recently, such complexes had only been identified spectroscopically in solution,[20] as in general they evolve to dimeric complexes of the type $[Rh(\mu\text{-}Cl)(CO)(phosphine)]_2$ with loss of CO. The stability of **2** probably results from the

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[14] The propensity of bis(diisopropylamino)phosphines to react with $[Rh(CO)_2(\mu\text{-}Cl)]_2$ strongly depends on the steric constraints of the third substituent of the phosphorus.[15] An excess of rhodium complex allows the coordination equilibration to be displaced and, thus, to complete the conversion of **1**.

[15] Dyer, P. W.; Fawcett, J.; Hanton, M. J.; Kemmitt, R. D. W.; Padda, R.; Singh, N. *J. Chem. Soc., Dalton Trans.* **2003**, 104.

[16] To an ether solution (5 mL) of [*o*-(trifluoromethyl)phenyl][bis(diisopropylamino)phosphino]diazomethane (**1**; 0.12 mmol) was added an ether solution (2 mL) of tetracarbonylbis(*μ*-chloro)dirhodium(I) ($[Rh(CO)_2(\mu\text{-}Cl)]_2$; 0.12 mmol) at −50 °C. After the mixture was stirred for 30 min at this temperature, complex **2** was obtained in quantitative yield (according to ^{31}P NMR spectroscopy). Orange crystals of **2** (38 mg, 52%) were obtained by cooling the ether solution to −80 °C. Mp: 75 °C dec.

[17] To an ether solution (5 mL) of [*o*-(trifluoromethyl)phenyl][bis(diisopropylamino)phosphino]diazomethane (**1**; 0.12 mmol) was added an ether solution (2 mL) of tetracarbonylbis(*μ*-chloro)dirhodium(I) ($[Rh(CO)_2(\mu\text{-}Cl)]_2$; 0.12 mmol) at room temperature. After the mixture was stirred for 30 min at this temperature, 1 mL of pentane was added and yellow crystals of **3** (60 mg, 64%) were obtained by cooling the solution to −20 °C. Mp: 63 °C dec.

[18] Selected spectroscopic data are as follows. For **2**: ^{19}F (376.5 MHz, C_7D_8, 223 K) δ 17.3; ^{31}P (162 MHz, C_7D_8, 223 K) δ 118.1 (d, $^1J_{PRh}$ = 162 Hz); $^{13}C\{^1H\}$ (100.6 MHz, C_7D_8, 223 K) δ 51.2 (dd, $^1J_{PC}$ = 32 Hz, $^2J_{CRh}$ = 7 Hz, CN_2), 181.8 (dd, $^2J_{PC}$ = 155 Hz, $^1J_{CRh}$ = 71 Hz, CO), 181.8 (dd, $^2J_{PC}$ = 16 Hz, $^1J_{CRh}$ = 71 Hz, CO). For **3a**: ^{31}P (162 MHz, C_7D_8, 223 K) δ 126.8 (d, $^1J_{PRh}$ = 220 Hz); $^{13}C\{^1H\}$ (100.6 MHz, C_7D_8, 223 K) δ 52.5 (dd, $^1J_{PC}$ = 6 Hz, $^2J_{CRh}$ = 10 Hz, CN_2), 179.4 (d, $^1J_{CRh}$ = 76 Hz, CO), 180.1 (d, $^1J_{CRh}$ = 76 Hz, CO), 183.8 (dd, $^2J_{PC}$ = 16 Hz, $^1J_{CRh}$ = 87 Hz, CO). For **3b**: ^{31}P (162 MHz, C_7D_8, 223 K) δ 127.8 (d, $^1J_{PRh}$ = 224 Hz).

[19] Crystal data for **2** and **3** are as follows. **2**: orthorhombic, space group $P2_12_12_1$; T = 173 K; a = 11.377(2) Å, b = 11.556(2) Å, c = 20.805(3) Å, V = 2735.2(6) Å^3, Z = 4, R1 ($I > 2\sigma(I)$) = 0.0439, wR2 (all data) = 0.0755 for 3930 unique reflections, 316 parameters, GOF = 0.999. **3**: triclinic, space group $P\bar{1}$; T = 173 K; a = 9.046(2) Å, b = 9.341(2) Å, c = 21.629(4) Å, α = 80.909(3)°, β = 83.124(4)°, γ = 82.532(4)°, V = 1780.2(5) Å^3, Z = 2, R1 ($I > 2\sigma(I)$) = 0.0530, wR2 (all data) = 0.1181 for 5049 unique reflections, 491 parameters, GOF = 0.984. Data for both structures were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. The structures were solved by direct methods using SHELXS-97[26] and refined with all data on F^2 using SHELXL-97.[27] All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were geometrically idealized and refined using a riding model. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-203087 (**2**), 203088 (**3**), and 203089 (**3′**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1 EZ, U.K. (fax, (+44)1223-336-033; email, deposit@ccdc.cam.ac.uk).

[20] (a) Rotondo, E.; Battaglia, G.; Giordano, G.; Cusmano, F. P. *J. Organomet. Chem.* **1993**, *450*, 245. (b) Uguagliati, P.; Deganello, G.; Belluco, U. *Inorg. Chim. Acta* **1974**, *9*, 203. (c) Steele, D. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1972**, 2161.

[21] (a) Orpen, A. G.; Brammer, B.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1. (b) Allen, F. H.; Kennard, O. 3D Search and Research Using the Cambridge Structural Database. *Chem. Design Automation News* **1993**, *8*(1), 1, 31−37. (c) Dyer, P. W.; Fawcett, J.; Hanton, M. J. Unpublished results.

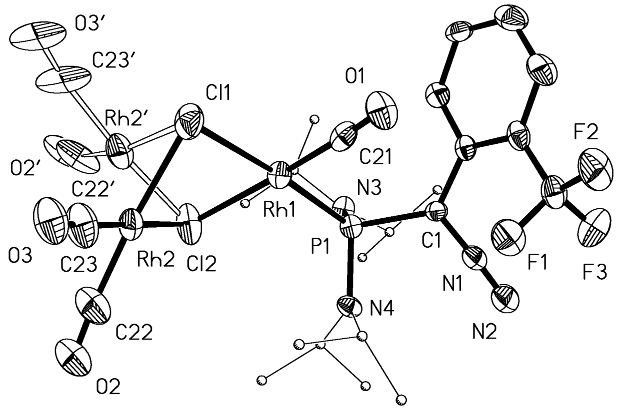

Figure 2. Molecular structure of **3** in the solid state. For clarity the hydrogen atoms are omitted and the isopropyl groups are simplified. Selected bond lengths (Å) and angles (deg): P1−C1 = 1.831(7), P1−Rh1 = 2.237(2), P1−N3 = 1.689(6), P1−N4 = 1.686(6), Rh1−Cl1 = 2.435(2), Rh1−Cl2 = 2.408(2), Rh1−C21 = 1.817(8); P1−C1−N1 = 115.5(5), P1−C1−C2 = 125.7(5), N1−C1−C2 = 118.3(6), C1−P1−N3 = 104.6(3), C1−P1−N4 = 100.2(3), C1−P1−Rh1 = 115.0(2), P1−Rh1−Cl1 = 175.75(8), P1−Rh1−Cl2 = 93.86(8), P1−Rh1−C21 = 94.1(2).

elevated basicity and poor π-acceptance of the phosphorus center of the bis(dialkylamino)phosphine moiety bound to rhodium.[15] Significantly, there is no interaction between the metal center and the diazo moiety.

The observation of three sets of signals for the carbonyl groups in the ^{13}C NMR spectrum for the major conformer of **3** was in favor of a dinuclear complex. The exact structure of both conformers was revealed by an X-ray diffraction study carried out on single crystals obtained from a diethyl ether/pentane solution of **3** at −20 °C. Complex **3** is a dinuclear rhodium(I) complex with two bridging chlorine atoms and a single coordinated (α-diazo)phosphine (Figure 2).[22]

The low-temperature ^{31}P NMR spectrum of a single crystal of **3** revealed that the same 4/1 ratio of conformers was present in the solid state and in solution. The two conformers differ in the geometry associated with the Rh1−Cl1−Cl2−Rh2 plane, with the major conformer adopting a "butterfly" arrangement about the Cl1−Cl2 vector, while for the minor conformer Rh1, Cl1, Cl2, and Rh2′ are near coplanar. As for **2**, the Rh1 center of **3** adopts a distorted-square-planar geometry ($\sum_{\text{angles}}$ = 366.16°), the Rh1−P bond distance in **3** being slightly shortened compared to that determined for **2** (**3**, 2.237(2) Å; **2**, 2.367(2) Å); the two Rh1−Cl bond distances are inequivalent, as expected (Rh−Cl(cis to P) = 2.408(2) Å and Rh−Cl(trans to P) = 2.435(2) Å). As in **2**, the aryl ring of the ligand is orientated perpendicularly to the square coordination plane of Rh1. Thus, it seems reasonable to suggest that the bulky *o*-trifluoromethyl group might impede rotation around the C$_{\text{ipso}}$−C$_{\text{diazo}}$ bond, giving rise to two conformers which differ as a consequence of syn and anti orientations of this CF$_3$ group toward the coordination plane about the second rhodium center. Although dinuclear monophosphine complexes analogous to **3** have been postulated as transient intermediates in the reaction of phosphines with tetracarbonylbis(μ-chloro)dirhodium(I), their structures have not been unambiguously determined.[20a]

The incorporation of **1** into the coordination sphere of rhodium without diazo decomposition is contrary to the reactivity often associated between diazo compounds and transition-metal salts. In many cases, even a catalytic amount of a transition-metal complex induces dinitrogen elimination,[23] only a very few complexes featuring an intact diazo moiety having been isolated.[24] The coordination of the (α-diazo)phosphine **1** via the phosphorus lone pair in preference to reaction at the diazo fragment is even more surprising, considering the presence of the bulky diisopropylamino groups.[25] Further studies into the coordination of (α-diazo)phosphines and on the use of the ensuing complexes as precursors for (phosphino)carbene complexes are currently in progress.

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Supporting Information Available: Text giving selected spectroscopic data for **2** and **3** and tables giving X-ray crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] An investigation of the molecular structure of the mesityl analogue of **3** has been undertaken, and all relevant crystallographic data are reported in the Supporting Information. An geometry identical with that observed for **3** was determined. It should be noted that the mesityl derivative **3′** was considerably more reactive than **3**, making its characterization much more difficult.

(23) Doyle, M. P.; McKervey, M. A. and Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley: New York, 1998; Chapter 2, pp 61−111.

(24) (a) Sutton, D. *Chem. Rev.* **1993**, *93*, 995. (b) Mizobi, Y.; Ishii, Y.; Hidai, M. *Coord. Chem. Rev.* **1995**, *139*, 281. (c) Dartiguenave, M.; Menu, M. J.; Deydier, E.; Dartiguenave, Y.; Siebald, H. *Coord. Chem. Rev.* **1998**, *178−180*, 623.

(25) Diazo compounds react with transition-metal fragments either by the carbon or by the terminal nitrogen atoms, with or without nitrogen elimination: *Diazo Chemistry*; Zollinger, H., Ed.; VCH: Weinheim, Germany, 1995; Vol. 2, pp 439−454.

(26) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(27) Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.