

Reaction of Tris(triethylphosphine)trimethylsilyldiazomethylrhodium(I) with Isocyanides. Synthesis and X-Ray Structure of the First 1*H*-1,2,3-Triazolato Complex with a Metal–Carbon Bond

Eric Deydier, Marie-Joëlle Menu, Michèle Dartiguenave* and Yves Dartiguenave

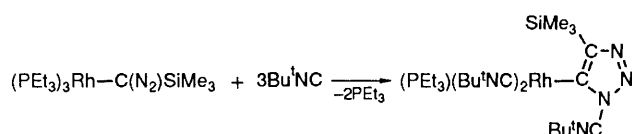
Laboratoire de Chimie Inorganique, Université P. Sabatier, 118 route de Narbonne F-31062 Toulouse-Cedex, France

Two new C-bonded 1*H*-1,2,3-triazolato rhodium(I) compounds have been synthesized from the 1,3-dipolar cycloaddition of the diazo complex $[\text{Rh}(\text{PEt}_3)_3\{\text{C}(\text{N}_2)\text{SiMe}_3\}]$ with isocyanides RNC (R = Bu^t and Buⁿ).

Organic diazoalkanes have been proven to be exceedingly useful in organic synthesis as precursors to carbenoid species or as reagents in heterocyclic synthesis via 1,3-dipolar cycloaddition.^{1a} By comparison, the chemical reactivity of diazoalkanes C-bonded to a transition metal is still underdeveloped. This is related to the fact that α -metallated diazoalkanes are few in number and still limited to osmium,² palladium,³ rhodium⁴ and nickel.⁵ Their carbenoid character has been illustrated in the case of the osmium, rhodium and nickel complexes where the transient α -metallated carbenes generated by photolysis have been successfully trapped by phosphine.^{2,5}

Isocyanides are well known for their ability to insert into metal–carbon bonds and to produce a variety of new compounds.⁶ Moreover, with organic diazoalkanes, they usually induce formation of ketylmines,^{1b} after N₂ extrusion. To our knowledge, only one example of a low yield synthesis of an organic triazole has been reported⁷ before. In this paper, we describe the 1,3-dipolar cycloaddition of isocyanides on the α -metallated diazomethyl complex: $[\text{Rh}(\text{PEt}_3)_3\{\text{C}(\text{N}_2)\text{SiMe}_3\}]$ which gave rise to the first 1*H*-1,2,3-triazolato ligand C-bonded to rhodium.

The reaction of $[\text{Rh}(\text{PEt}_3)_3\{\text{C}(\text{N}_2)\text{SiMe}_3\}]$ (300 mg; 0.53 mmol) with an excess of RNC (in the ratio 1:4) at room temperature in C₆H₆ afforded **1** (R = Bu^t) in a high yield reaction under mild conditions (Scheme 1).



Scheme 1

Air-sensitive yellow crystals of **1**, *trans*-(1-*tert*-butyl-4-trimethylsilyl-1*H*-1,2,3-triazolato)triethylphosphinebis(*tert*-butyl isocyanide)rhodium(I) were obtained by slow crystallization from cyclopentane. When BuⁿNC was used, only one PEt₃ ligand was substituted by isocyanide and (PEt₃)₂-(BuⁿNC)Rh[$\overline{\text{C}}(\text{SiMe}_3)\text{N}_2\text{N}(\text{Bu}^n)$] was precipitated as yellow crystals. In the infrared, they display one $\bar{\nu}(\text{C}\equiv\text{NBu}^t)$ at 2100 cm⁻¹ for **1** (Nujol mull) and at 2113 cm⁻¹ for **2** (in C₆H₆), typical of terminal isocyanide. As evidenced by ³¹P, ¹H and ¹³C NMR spectroscopy, only one phosphine and two magnet-

ically equivalent isocyanide ligands were present in **1**[†] while in **2**[‡] two *trans*-PEt₃ and one BuⁿNC ligands were observed. In order to characterize unambiguously **1** and because there is no precedent of C-bonded 1*H*-1,2,3 triazole, a single crystal X-ray analysis was undertaken.[‡] The ORTEP view is illustrated in Fig. 1, along with the atom numbering and the pertinent parameters. **1** consists of monomeric molecules. The geometry around Rh is square planar, with two *trans-tert*-butyl isocyanides, one triethylphosphine and the C-bonded 1*H*-1,2,3 triazolato ligand.

The P(1)C(20)C(30)RhC(1) core is only slightly distorted from a square planar geometry, the angles around rhodium being 171.9(8) and 176.7(6)°. The heterocycle is planar, this plane being nearly perpendicular to the P(1)C(20)C(30)RhC(1) plane [dihedral angle, 87.4(6)°]. Disorder was observed in the isocyanide ligands and in the ethyl substituents of the phosphine. The distances and angle values in the triazole are as expected for C=C, C–N, N–N and N=N bond lengths and CCN, CNN and NNN angles in an heteropentacycle.⁹ The Rh–C and Rh–P distances are consistent with the usual values reported for Rh^I–CNR and Rh^I–PR₃ bonds.¹⁰ The two terminal *tert*-butyl isocyanides are slightly

[†] Selected spectroscopic data for **1**: ³¹P{¹H} NMR (C₆D₆): δ 27 (d, $J_{\text{Rh-P}}$ 113 Hz); ¹H NMR (C₆D₆): δ 0.96 [(CH₃)₃CNC], 1.00 (CH₃)₃Si], 1.22 [(CH₃CH₂)₃P], 1.57 [(MeCH₂)₃P], 2.28 [(CH₃)₃CNC]. ¹³C{¹H} NMR (C₆D₆): δ 2.09 [(CH₃)₃Si], 9.0 [(CH₃CH₂)₃P], 21.1 [d, (MeCH₂)₃P, $J_{\text{C-P}}$ 21.9 Hz], 30.08 [(CH₃)₃CNC], 32.89 [(CH₃)₃CNC], 55.57 [Me₃CNC], 57.25 [Me₃CNC]. Mass spectrometry (EI, 70 eV): 583 (M⁺); 555 (M⁺ – N₂); 472 [M⁺ – N₂ – (Bu^tNC)].

[‡] ³¹P{¹H} NMR (C₆D₆): δ 18 (d, $J_{\text{P-Rh}}$ 137 Hz); ¹H NMR (C₆D₆): δ 1.16 [(CH₃CH₂)₃P], 1.48 [(MeCH₂)₃P], 0.88 [Me₃Si]. ¹³C{¹H} NMR (C₆D₆): δ 13.61 [CH₃(CH₂)₃NC], 14.55 [CH₃(CH₂)₃NC], 20.25 [MeCH₂(CH₂)₂NC], 21.78 [MeCH₂(CH₂)₂NC], 31.97 [MeCH₂CH₂CH₂NC], 33.86 [MeCH₂CH₂CH₂NC], 43.33 [Me(CH₂)₂CH₂NC], 53.47 [Me(CH₂)₂CH₂NC], 9.1 [(CH₃CH₂)₃P], t, 19.3 [(MeCH₂)₃P, J_{PC} 12 Hz], 2.35 [Me₃Si].

[‡] Crystal data for **1**: monoclinic, $P2_1/c$, $a = 11.914(4)$, $b = 10.092(4)$, $c = 28.34(2)$ Å, $\beta = 96.16(5)^\circ$, $Z = 4$, $V = 3398$ Å³, $D_c = 1.155$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 5.36$ cm⁻¹, $T = 20 \pm 2^\circ\text{C}$, $R = 0.0943$ ($R_w = 0.1030$) for 2630 reflections $I > 3\sigma(I)$ measured on an Enraf-Nonius CAD-4 diffractometer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

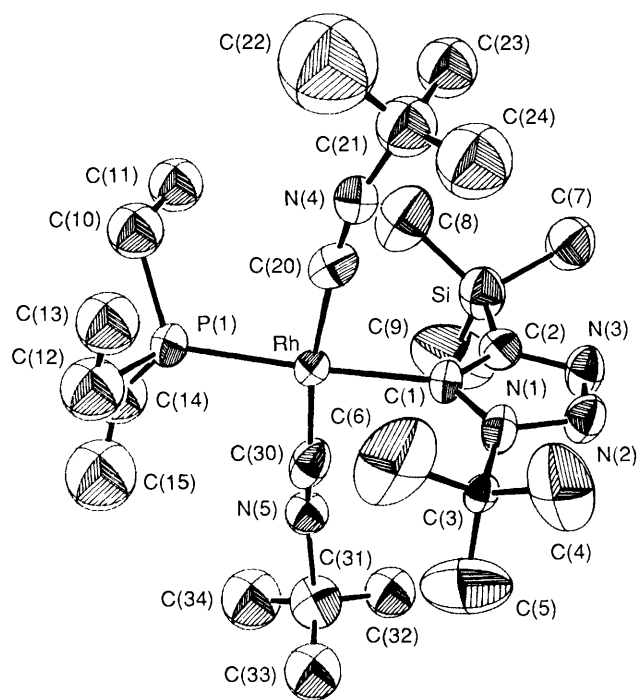


Fig. 1 ORTEP view of the $[\text{Rh}(\text{PEt}_3)(\text{Bu}^t\text{NC})_2]_2[\overline{\text{CC}(\text{SiMe}_3)\text{N}_2\text{N}-(\text{Bu}^t)}]$ **1** molecule and atoms labelling scheme. Hydrogen atoms and disorder are omitted for clarity. Ellipsoids are drawn at 50% probability. Main bond distances (Å): Rh–C(20) 1.84(2); Rh–C(30) 1.82(2); Rh–C(1) 2.10(2); Rh–P(1) 2.270(6); C(1)–C(2) 1.39(3); C(2)–N(3) 1.42(3); N(3)–N(2) 1.26(2); N(2)–N(1) 1.38(2); N(1)–C(1) 1.41(2); bond angles (°): C(2)–Rh–C(30) 171.9(8); P(1)–Rh–C(1) 176.7(6); P(1)–Rh–C(20) 93.1(6); P(1)–Rh–C(30) 95.0(6); C(1)–Rh–C(20) 84.4(8); C(1)–Rh–C(30) 87.5(8); Rh–C(1)–C(2) 128(1); Rh–C(1)–N(1) 127(1); C(1)–C(2)–N(3) 106(2); C(2)–N(3)–N(2) 110(2); N(3)–N(2)–N(1) 111(2); N(2)–N(1)–C(1) 108(2); N(1)–C(1)–C(2) 106(2).

bent towards the heterocycle probably because of the steric requirements of the other ligands.

In conclusion, this reaction develops a new synthesis of functional triazoles. These molecules, till now, were obtained

by reaction of unsaturated organic compounds with organic azides¹¹ and in addition their reactions with metallic complexes were limited to N-bonded derivatives.¹² Work is now in progress to establish the mechanism of this reaction.

Received, 1st March 1991; Com. 1/00973G

References

- (a) S. Patai, *The Chemistry of Diazonium and Diazo Groups*, Part I and II, Wiley, New York, 1978; (b) ch. 18, p. 859.
- M. A. Gallop, T. C. Jones, E. F. Rickard and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1984, 1002; M. A. Gallop and W. R. Roper, *Adv. Organomet. Chem.*, 1986, **25**, 156.
- S. I. Murahashi, Y. Kitani, T. Uno, T. Hosokawa, K. Miki, T. Yinezawa and N. Kasai, *J. Chem. Soc., Chem. Commun.*, 1979, 450; *Organometallics*, 1986, **5**, 356.
- M. J. Menu, P. Desrosiers, M. Dartiguenave, Y. Dartiguenave and G. Bertrand, *Organometallics*, 1987, **6**, 1822.
- H. König, M. J. Menu, M. Dartiguenave, Y. Dartiguenave and H. F. Klein, *J. Am. Chem. Soc.*, 1990, **112**, 5351 and work to be published.
- Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, 1974, **13**, 438; D. S. Gill, P. K. Barker, M. Green, K. E. Paddick, M. Murray and J. W. Welch, *J. Chem. Soc., Chem. Commun.*, 1981, 986; L. D. Durfee and I. P. Rothwell, *Chem. Rev.*, 1988, **88**, 1059; E. Carmona, P. Palma, M. Paneque and M. L. Poveda, *Organometallics*, 1990, **9**, 583.
- M. Muramatsu, N. Obata and T. Takizawa, *Tetrahedron Lett.*, 1973, **23**, 2136.
- P. Dufour, M. Dartiguenave, Y. Dartiguenave and A. L. Beauchamp to be submitted and references cited therein.
- D. Barton and W. D. Ollis, in *Comprehensive Organic Chemistry*, ed., P. G. Sammes, Pergamon, Oxford, 1979, vol. iv ch. 7, p. 361; L. Parkanyi, A. Kalman, G. Argay and J. Schwartz, *Acta Crystallogr. Sect. B*, 1977, **33**, 3102; Y. Nagawa, M. Goto, K. Honda and H. Nakanishi, *Acta Crystallogr. Sect. C*, 1987, **43**, 147.
- W. D. Jones and E. T. Hessel, *Organometallics*, 1990, **9**, 718.
- G. L'abbé, A. Vandendriessche and S. Toppet, *Tetrahedron*, 1988, **44**, 3617; L. Benati, P. Montevecchi and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1989, 2235.
- L. Goodrich Purnell, J. Causey Shepherd and D. J. Hodgson, *J. Am. Chem. Soc.*, 1975, **97**, 2376; W. Rigby, P. M. Bailey, J. A. McCleverty and P. M. Maitlis, *J. Chem. Soc.*, 1979, 371; J.R. Olson, M. Yamauchi and W. M. Butler, *Inorg. Chem. Acta*, 1985, **99**, 121; W. S. Sheldrick and P. Bell, *Z. Naturforsch., Teil B*, 1987, **42**, 195.