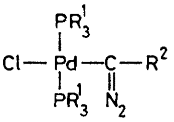
Synthesis and Structure of α-Diazomethyl Palladium σ-Complexes; *X*-Ray Crystal Structure of Chloro[diazo(ethoxycarbonyl)-methyl]bistriphenylphosphinepalladium

By Shun-Icni Murahashi,* Yasuo Kitani, and Takahiro Hosokawa
(*Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka, 560, Japan*)
and Kunio Miki and Nobutami Kasai*
(*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka, 555, Japan*)

Summary Syntheses of $(R^1{}_3P)_2ClPdC(N_2)R^2$ (**1**) and $(R^1{}_3P)_2$-$Pd[C(N_2)R^2]_2$ (**2**), the first α-diazomethyl complexes of group 8 transition metals, are reported; their structures were determined from spectroscopic data and by *X*-ray crystallography of chloro[diazo(ethoxycarbonyl)methyl]-bistriphenylphosphinepalladium (**1a**).

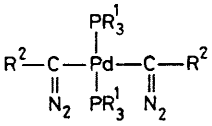
α-Metallodiazo-compounds are of interest as precursors of carbene and carbyne complexes and as intermediates in the synthesis of substituted diazo-compounds.[1] However, the diazo-complexes of this type reported so far are limited to those of non-transition metals[2] and group 1B[3] and 2B[2] transition metals. We report the synthesis of the complexes (**1**) and (**2**) and their structural characterization by *X*-ray analysis of (**1a**) and spectroscopy. Complexes (**1**) and (**2**) are the first α-diazomethyl complexes of group 8 transition metals, which are good catalysts for the decomposition of diazo-compounds.[1]



$\mathrm{Cl{-}Pd(PR^1_3)_2{-}C(=N_2){-}R^2}$

(1)

a, R^1 = Ph, R^2 = CO_2Et
b, R^1 = Ph, R^2 = C(O)Me



$\mathrm{R^2{-}C(=N_2){-}Pd(PR^1_3)_2{-}C(=N_2){-}R^2}$

(2)

a, R^1 = Ph, R^2 = CO_2Et
b, R^1 = Et, R^2 = CO_2Et
c, R^1 = Ph, R^2 = C(O)Me
d, R^1 = Et, R^2 = Ph

TABLE. Physical data and yields of (**1**) and (**2**).

Complex	Yield[a]/%	Colour	M.p. (decomp.) /°C	I.r. $\nu(CN_2)$[d] /cm^{-1}	$^{13}C\{^1H\}$N.m.r.[e] $\delta^{13}C$(diazo)/p.p.m.
(**1a**)	39	Red	146—148	2035	37·63 (8·8)
(**1b**)	22	Red	*ca.* 142	2010	—
(**2a**)	21[b]	Orange	138—139	2025	36·34 (11·8)
(**2b**)	73[c](14)[b]	Orange	125—127	2025	32·82 (11·8)
(**2c**)	27[b]	Orange	137—138	2005	—
(**2d**)	58[c]	Violet	110—111	1985	37·05 (11·8)

[a] Yields after purification by chromatography and recrystallization. [b] Method B. [c] Method A. [d] In Nujol. [e] Measured in CD_2Cl_2 under argon; chemical shifts are relative to Me_4Si. $^2J_{P-C}$ (in Hz) in parentheses.

Typical examples of (**1**) and (**2**), which are air-stable in the solid state but decompose in nondeoxygenated solutions, are summarized in the Table. Complexes (**1**) were prepared by treatment of $(PPh_3)_2PdCl_2$ with $Hg[C(N_2)R^2]_2$ in dry benzene at room temperature under argon, and purified by Florisil short column chromatography (argon; CH_2Cl_2) in the dark, followed by recrystallization (CH_2Cl_2–hexane). Complexes (**2**) were prepared by similar treatment of $Pd(PR^1_3)_2Cl_2$ with $LiC(N_2)R^2$† at −78 °C (method A) and also by oxidative addition of $Hg[C(N_2)R^2]_2$ to $(PR^1_3)_4Pd$ (method B).

In the $^{13}C\{^1H\}$ n.m.r. spectra of (**1**) and (**2**), the diazo-carbon resonances appear at δ 33—38 p.p.m. as a triplet ($^2J_{P-C}$ 9—12 Hz), suggesting that this atom is α-bonded to Pd. The i.r. spectra of (**1**) and (**2**) exhibit strong $\nu(CN_2)$ absorptions at 1985—2035 cm^{-1}, which are shifted by *ca.* 50—90 cm^{-1} to longer wavelength compared with the parent diazo-compounds, $RCH(N_2)$ [R = CO_2Et, 2110; R = C(O)Me, 2100; and R = Ph, 2037 cm^{-1}], indicating a decrease in the triple bond character of the nitrogen–nitrogen bond. The structure of (**1a**) has been determined by *X*-ray diffraction.

Crystal data: $C_{40}H_{35}ClN_2O_2P_2Pd$, $M = 779·5$, monoclinic, $F(000) = 1592$, space group $P2_1/c$ (No. 14), $a = 11·973(2)$, $b = 29·710(6)$, $c = 10·310(2)$ Å, $\beta = 94·71(2)°$, $U = 3656·3(10)$ Å^3, $Z = 4$, $D_c = 1·416$ g cm^{-3}, μ(Mo-K_α) = 6·98 cm^{-1}. Intensity data ($2\theta < 50·5°$) were collected on a Rigaku four-circle diffractometer (Mo-K_α radiation; Zr-filter; θ—2θ scan). The structure was solved by the heavy-atom method and refined anisotropically by block-diagonal least-squares to $R = 0·084$ for 3977 reflexions [$F > 3\sigma(F)$].‡

The geometry around the Pd atom is square-planar. The least-squares plane through the almost planar α-diazomethyl group (N_2CCO_2Et) [except for C(4)] inclines at 81·6° to the co-ordination plane of Pd. The Pd–C(1) bond length [2·010(11) Å] is as expected for a Pd^{II}–$C(sp^2)$ bond, and the C(1)–N(1)–N(2) angle is almost linear [177·0(13)°]. It is noteworthy that the N(1)–N(2) bond length [1·17(2) Å] is 0·04—0·07 Å longer, and the C(1)–N(1) bond length [1·27(2) Å] is 0·04–0·09 Å shorter than the corresponding N–N and N–C bond lengths in diazomethane[4] and diazoketones.[5] This result, which is compatible with the i.r. spectral data, shows that the resonance structure (**3**) plays an important contribution in the complex (**1**).[6]

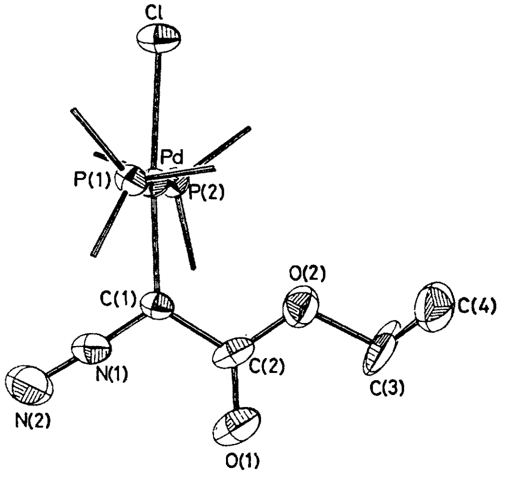


FIGURE. Molecular structure of $[PdCl(N_2CCO_2Et)(PPh_3)_2]$. Thermal ellipsoids correspond to 30% probability levels. Six phenyl groups of the triphenyl phosphine ligands are omitted for clarity. Selected bond lengths and bond angles are: Pd–Cl 2·345(4), Pd–P(1) 2·324(3), Pd–P(2) 2·321(3), Pd–C(1) 2·010(11), N(1)–N(2) 1·17(2), C(1)–N(1) 1·27(2), C(1)–C(2) 1·45(2), C(2)–O(1) 1·22(2), C(2)–O(2) 1·32(2), O(2)–C(3) 1·47(3), C(3)–C(4) 1·43(4) Å; C(1)–N(1)–N(2) 177·0(13), Pd–C(1)–N(1) 122·1(9), Pd–C(1)–C(2) 124·3(9), and N(1)–C(1)–C(2) 113·5(11)°.

$$>C=\overset{+}{N}=\overset{-}{N} \longleftrightarrow >\overset{-}{C}-\overset{+}{N}\equiv N$$

(**3**) (**4**)

(*Received*, 13*th February* 1979; *Com.* 143.)

---

† The lithiation products of $RCH(N_2)$ with $LiN(Pr^i)_2$ in tetrahydrofuran at −78 °C were used *in situ*.

‡ Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] W. A. Herrmann, *Angew. Chem. Internat. Edn.*, 1978, **17**, 800, and references therein.

[2] M. F. Lappert and J. S. Poland, *Adv. Organometallic Chem.*, 1970, **9**, 397; A. Fadini, E. Glozback P. Krommers, and J. Lorberth, *J. Organometallic Chem.*, 1978, **149**, 297.

[3] U. Schöllkopf, *Chem. Ber.*, 1969, **102**, 488.

[4] A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature*, 1958, **181**, 1000.

[5] G. B. Ansell, *J. Chem. Soc.* (*B*), 1969, 729; D. J. Abraham, T. G. Cochran, and R. D. Rosenstein, *J. Amer. Chem. Soc.*, 1971, **93**, 6279; H. Hakon and K. T. Black, *Acta Cryst.*, 1972, **B28**, 3632; A. F. Cameron, H. J. Hair, and D. G. Morris, *J.C.S. Perkin II*, 1972, 1331.

[6] R. O. Duthaler, H. G. Förster, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1978, **100**, 4974.