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# Neutral and cationic monocarbonyl derivatives of palladium(II). X-ray crystal structure of [Pd(8-mq)(CO)(SPPh<sub>3</sub>)]ClO<sub>4</sub>

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Abstract—Carbonylation of  $[Pd(8-mq)(OCMe_2)_x]ClO_4$  (8-mq = 8-quinolylmethyl-C,N) in  $CH_2Cl_2/Me_2CO$  at low temperature gave  $[Pd(8-mq)(OCIO_3)(CO)]$ . Reactions of  $[Pd(8-mq)(OCIO_3)(CO)]$  with anionic  $(CI^-, Br^-, I^-)$  or neutral (SPPh<sub>3</sub>, SPMe<sub>2</sub>Ph) nucleophiles in a 1 : 1 molar ratio resulted in the displacement of the weakly coordinated OCIO<sub>3</sub><sup>-</sup> group and the formation of the corresponding neutral [Pd(8-mq)(X)(CO)] (X = Cl, Br, I) or cationic  $[Pd(8-mq)(CO)L]ClO_4$  (L = SPPh<sub>3</sub>, SPMe<sub>2</sub>Ph) carbonyl complexes. The cationic complexes,  $[Pd(8-mq)(CO)L]ClO_4$ , were synthesized by the reaction of  $[Pd(8-mq)(OCIO_3)(SPPh_3)]$  or  $[Pd(8-mq)(\mu-SPMe_2Ph)]_2(ClO_4)_2$  with CO. The X-ray structure of a cationic palladium carbonyl derivative,  $[Pd(8-mq)(CO)(SPPh_3)]ClO_4$ , is reported. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: carbonyl; palladium; cationic; cyclometallated.

Palladium compounds have been used as catalysts in some of the most important homogeneous catalytic processes involving CO [1]. Insertion of CO in a Pd-C  $\sigma$ -bond is an elementary step which should occur through intermediates in which the coordinated carbonyl and organic groups are located in the cis position [2]. This ability to form acyl derivatives adds to the general tendency of Pd<sup>II</sup> compounds to be reduced to lower oxidation states by carbon monoxide and to the lability of the Pd—CO bond, justifying the small number of organocarbonylpalladium(II) complexes that have been reported and characterized [3]. Most of them have been structurally studied on the basis of spectroscopic data (mainly IR) and only very recently have the crystal structures of seven such compounds:  $[PdX_3(CO)]^-$  (X = Cl, Br) [4],  $[PPh_3(CH _{2}$ Ph)][Pd(C<sub>6</sub>H<sub>3</sub>Me-2,NO<sub>2</sub>-6)Cl<sub>2</sub>(CO)] [5],  $[Pd(\eta^3 -$ C<sub>4</sub>H<sub>7</sub>)(SnCl<sub>3</sub>)(CO)] [6], [2-(CO)-2-(PPh<sub>3</sub>)-closo-2,1- $PdTeB_{10}H_9(PPh_3)BF_4$  [7], [cis-Pd(SO<sub>3</sub>F)<sub>2</sub>(CO)<sub>2</sub>] [8] and [(phen)Pd (C(O)CH<sub>3</sub>)(CO)]  $Ar'_4B \cdot CH_2Cl_2$  [9], been reported.

The main synthetic routes for the preparation of

palladium carbonyls involve the displacement of weakly coordinated ligands by CO [9,10]. Working on C,N-cyclometallated compounds of Pd<sup>II</sup>, we have prepared several complexes with this kind of ligand: [Pd(8-mq)(NCMe)\_2]ClO<sub>4</sub> [11], [Pd(8-mq)(OCIO\_3) (SPPh\_3)] [12], [Pd(8-mq)( $\mu$ -SPMe\_2Ph)]\_2(ClO\_4)\_2 and [Pd(8-mq)(OCMe)\_x]<sup>+</sup> (*in situ*), and we have found that they are very good precursors for the preparation of new carbonyl complexes of Pd<sup>II</sup>.

Herein we report the synthesis and characterization of some cationic and neutral thermally stable carbonylpalladium(II) complexes, as well as the molecular structure of one of the cationic derivatives, [Pd(8mq)(CO)(SPPh<sub>3</sub>)]ClO<sub>4</sub>.

### **EXPERIMENTAL**

#### General procedures

Infrared spectra were recorded on a Perkin–Elmer 883 IR spectrometer using Nujol mulls between polyethylene plates. NMR spectra were recorded on a Varian Unity-300 or a Bruker ARX-300 spectrometer in CDCl<sub>3</sub> or acetone- $d_6$ , using the solvent signal as an

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internal standard for <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H}, and H<sub>3</sub>PO<sub>4</sub> (85%) as external reference for <sup>31</sup>P {<sup>1</sup>H}. Elemental analyses were performed on a Perkin–Elmer 240-B microanalyser. Molar conductivity measurements were performed on a Philips P.W. 9509 digital conductimeter in approximately  $5 \times 10^{-4}$  M acetone solutions. [Pd(8-mq)(OClO<sub>3</sub>)(SPPh<sub>3</sub>)] [12] and [Pd(8-mq)( $\mu$ -Cl)]<sub>2</sub> [13] were prepared by literature methods.

#### $[Pd(8-mq)(\mu-1)]_2$

[Pd(8-mq)( $\mu$ -Cl)]<sub>2</sub> (0.200 g, 0.352 mmol) and AgClO<sub>4</sub> (0.146 g, 0.704 mmol) were stirred in acetone (20 cm<sup>3</sup>) for 1 h, and then the AgCl formed was filtered off. NBu<sub>4</sub>I (0.260 g, 0.704 mmol) was added to the resulting solution giving rise to the precipitation of a yellow solid, which was separated by filtration, washed with acetone and vacuum dried (0.212 g, 80% yield). Found: C, 32.0; H, 1.8; N, 3.5. Calc. for C<sub>20</sub>H<sub>16</sub>I<sub>2</sub>N<sub>2</sub>Pd<sub>2</sub>: C, 32.0; H, 2.2; N, 3.7%. IR (Nujol, cm<sup>-1</sup>): 8-mq 1591 m, 1581 s, 1506 vs, 1071 s, 1052 vs, 816 vs, 776 vs, 751 vs, 666 m.

#### $[Pd(8-mq)(\mu-SPMe_2Ph)]_2(ClO_4)_2$

[Pd(8-mq)(μ-Cl)]<sub>2</sub> (0.120 g, 0.211 mmol) and AgClO<sub>4</sub> (0.087 g, 0.422 mmol) were stirred in THF (20 cm<sup>3</sup>) for 30 min and then the AgCl formed was filtered off. SPMe<sub>2</sub>Ph (0.72 g, 0.422 mmol) was added to the resulting solution and the mixture was stirred for 30 min. Following this, the solvent was concentrated to *ca* 5 cm<sup>3</sup> and the precipitated yellow solid was separated by filtration (0.197 g, 90% yield). Found: C, 41.9; H, 3.7; N, 2.9. Calc. for  $C_{36}H_{38}Cl_2N_2O_8P_2Pd_2S_2$ : C, 41.7; H, 3.7; N, 2.7%. Molar conductivity (S cm<sup>2</sup> mol<sup>-1</sup>): 291. IR (Nujol, cm<sup>-1</sup>): 8-mq 1598 w, 1500 vs, 832 s, 782 m, 778 m, 758 s; SPMe<sub>2</sub>Ph 950 s, 912 vs, 745 vs, 688 s, 518 s, 523 s [ν(P—S)]; ClO<sub>4</sub><sup>-1</sup> 1100 vs, 620 s. <sup>31</sup>P {<sup>1</sup>H} NMR: δ 41.99 (s).

#### [Pd(8-mq)(OClO<sub>3</sub>)(CO)] (1)

[Pd(8-mq)(μ-Cl)]<sub>2</sub> (0.200 g, 0.352 mmol) and AgClO<sub>4</sub> (0.146 g, 0.704 mmol) were stirred in acetone (20 cm<sup>3</sup>) for 30 min, and the AgCl formed was filtered off. The solution was evaporated to *ca* 2 cm<sup>3</sup>, then 5 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> was added and carbon monoxide was gently bubbled through the resulting pale yellow suspension at  $-60^{\circ}$ C for 10 min. Addition of diethyl ether (25 cm<sup>3</sup>) to the suspension afforded a white solid, which was filtered off and dried *in vacuo.* 1 (0.238 g, 90% yield). Found: C, 34.8; H, 1.8; N, 3.6. Calc. for C<sub>11</sub>H<sub>8</sub>ClNO<sub>5</sub>Pd (1): C, 35.1; H, 2.1; N, 3.7%. Molar conductivity (S cm<sup>2</sup> mol<sup>-1</sup>): 156. IR (Nujol, cm<sup>-1</sup>): 8mq: 1596 w, 1514 vs, 825 s, 788 m, 768 s; OClO<sub>3</sub><sup>-</sup> 1144 vs, 1025 vs, 908 vs, 624 s, 612 m; ν(CO) 2140 vs. [Pd(8-mq)X(CO)] [X = Cl (2a), Br (2b), I (2c)].

X = Cl (2a). (a) Method 1. To a suspension of [Pd(8-mq)(OClO<sub>3</sub>)(CO)] (1) (0.175 g, 0.465 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was added an equimolar amount of [PBzPh<sub>3</sub>]Cl (0.180 g, 0.465 mmol) at room temperature. The mixture was stirred for 3 min and filtered to remove a small amount of suspended solid. The addition of cold Pr<sup>i</sup>OH (80 cm<sup>3</sup>,  $-30^{\circ}$ C) to the resulting solution rendered a white solid which was identified by IR spectroscopy as 2a, with a small amount of [Pd(8-mq)( $\mu$ -Cl)]<sub>2</sub> as an impurity.

(b) Method 2. CO was gently bubbled through a suspension of  $[Pd(8-mq)(\mu-Cl)]_2$  (0.420 g, 0.739 mmol) in 12 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> at  $-30^{\circ}$ C for 15 min. After filtration, the resulting solution was added to cold nhexane (90 cm<sup>3</sup>,  $-30^{\circ}$ C) affording a white solid which was filtered off and dried in vacuo. 2a, (0.16 g, 35% yield). Found: C, 42.1; H, 2.2; N, 4.3. Calc. for C11H8CINOPd: C, 42.3; H, 2.6; N, 4.5%. IR (Nujol, cm<sup>-1</sup>): 8-mq 1593 w, 1509 vs, 826 s, 787 s, 768 s, 694 m; v(Pd-Cl) 290 m; v(CO) 2112 vs (solid), 2121 (CH<sub>2</sub>Cl<sub>2</sub> solution). <sup>1</sup>H NMR (proton labelling is shown in Fig. 1):  $\delta$  9.48 (d, H1,  ${}^{3}J_{1-2} = 5.04$  Hz), 8.38 (d, H3,  ${}^{3}J_{3-2} = 8.30$  Hz), 7.72 (d, H6,  ${}^{3}J_{5-6} = 7.90$  Hz), 7.65 (d, H4,  ${}^{3}J_{4.5} = 7.1$  Hz), 7.58 (pt, H5), 7.54 (dd, H2), 3.89 (s, -CH<sub>2</sub>-Pd). <sup>13</sup>C NMR:  $\delta$  151.83, 150.59, 144.24, 139.66, 130.05, 129.11, 128.57, 124.88, 121.67 (C<sub>9</sub>H<sub>6</sub>N), 30.14 (-CH<sub>2</sub>-Pd); 176.98 (CO).

X = Br (2b). To a suspension of [Pd(8mq)(OClO<sub>3</sub>)(CO)] (1) (0.049 g, 0.131 mmol) in  $CH_2Cl_2$  (10 cm<sup>3</sup>) an equimolar amount of NBu<sub>4</sub>Br (0.042 g, 0.131 mmol) was added. The mixture was stirred at room temperature for 5 min and filtered to remove a small amount of suspended solid. The resulting solution was added to cold <sup>i</sup>PrOH (60 cm<sup>3</sup>,  $-30^{\circ}$ C) giving rise to pure **2b** (0.023 g, 50% yield). Found: C, 37.1; H, 2.2; N, 3.9. Calc. for C<sub>11</sub>H<sub>8</sub>BrNOPd: C, 37.1; H, 2.3; N, 3.9%. IR (Nujol, cm<sup>-1</sup>): 8-mq 1593 w, 1510 vs, 823 s, 776 s, 764 m, 689 m; v(CO) 2108 vs (solid), 2117 (CH<sub>2</sub>Cl<sub>2</sub> solution). <sup>1</sup>H NMR:  $\delta$  9.67 (dd, H1,  ${}^{3}J_{1-2} = 5.09$  Hz,  ${}^{4}J_{1-3} = 1.42$  Hz), 8.38 (dd, H3,  ${}^{3}J_{3\cdot2} = 8.32$  Hz), 7.73 (dd, H6,  ${}^{3}J_{5\cdot6} = 7.80$  Hz,  ${}^{4}J_{4\cdot6}$ = 1.09 Hz), 7.66 (dd, H4,  ${}^{3}J_{4-5} = 7.1$  Hz), 7.59 (pseudo t, H5), 7.55 (dd, H2), 3.99 (s, -CH<sub>2</sub>-Pd). <sup>13</sup>C



NMR  $\delta$ : 152.24, 151.86, 144.29, 139.61, 130.17, 129.23, 128.60, 125.00, 121.99 (C<sub>9</sub>H<sub>6</sub>N), 32.52 (-CH<sub>2</sub>-Pd); 177.65 (CO).

X = I(2c). (a) Method 1. To a suspension of [Pd(8-mq)(OClO<sub>3</sub>)(CO)] (1) (0.135 g, 0.360 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) an equimolar amount of PMe<sub>3</sub>PhI (0.100 g, 0.360 mmol) was added at room temperature. The mixture was stirred for 5 min and filtered to remove a small amount of suspended solid. Addition of Pr'OH (50 cm<sup>3</sup>) to the resulting solution afforded a yellow solid which was separated by filtration and vacuum dried. The solid was identified by IR spectroscopy as **2c** with a small amount of [Pd(8-mq)( $\mu$ -I)]<sub>2</sub> as an impurity.

(b) Method 2. CO was gently bubbled through a suspension of  $[Pd(8-mq)(\mu-I)]_2$ . (0.150 g, 0.200 mmol) in 20 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> at  $-5^{\circ}$ C for 30 min. After filtration of the suspended solid the resulting solution was added to cold n-hexane (80 cm<sup>3</sup>,  $-30^{\circ}$ C) affording 2c (yield 0.10 g, 62%). Found: C, 32.6; H, 1.9; N, 3.4. Calc. for C<sub>11</sub>H<sub>8</sub>INOPd: C, 32.7; H, 2.0; N, 3.5%. IR (Nujol, cm<sup>-1</sup>): 8-mq 1592 w, 1510 vs, 822 s, 774 vs, 761 m, 682 m; v(CO): 2103 vs (solid), 2110 (CH<sub>2</sub>Cl<sub>2</sub> solution). <sup>1</sup>H NMR:  $\delta$  9.89 (dd, H1, <sup>3</sup>J<sub>1-2</sub> = 5.04 Hz,  ${}^{4}J_{1-3} = 1.30$  Hz), 8.35 (dd, H3,  ${}^{3}J_{3-2} = 8.32$  Hz), 7.71 (dd, H6,  ${}^{3}J_{5.6} = 7.85$  Hz,  ${}^{4}J_{4.6} = 1.0$  Hz), 7.64 (dd, H4,  ${}^{3}J_{4-5} = 7.1$  Hz), 7.60 (pseudo t, H5), 7.49 (dd, H2), 4.08 (s, -CH<sub>2</sub>-Pd). <sup>13</sup>C NMR:  $\delta$  151.82, 151.15, 144.64, 139.34, 130.36, 129.40, 128.76, 125.08, 122.44  $(C_9H_6N)$ , 35.92 (-CH<sub>2</sub>-Pd); 179.22 (CO).

#### $[Pd(8-mq)(CO)(SPPh_3)]ClO_4$ (3a)

(a) Method 1. SPPh<sub>3</sub> (0.109 g, 0.372 mmol) was added to a CH<sub>2</sub>Cl<sub>2</sub> suspension (5 cm<sup>3</sup>) of 1 (0.14 g, 0.372 mmol) to give a pale yellow solution. The mixture was stirred for 2 min at room temperature and then 15 cm<sup>3</sup> of n-hexane was added. The resulting pale yellow precipitate was filtered off and dried *in vacuo* to give **3a**, (0.200 g, 80% yield).

(b) Method 2. Carbon monoxide was gently bubbled through a  $CH_2Cl_2$  (1.5 cm<sup>3</sup>) solution of [Pd(8mq)(OClO<sub>3</sub>)(SPPh<sub>3</sub>)] (0.143 g, 0.223 mmol) for 5 min at  $-30^{\circ}$ C. Addition of n-hexane (20 cm<sup>3</sup>) rendered a pale yellow precipitate, 3a (0.105 g, 70% yield). Found: C, 51.7; H, 3.1; N, 2.1. Calc. for  $C_{29}H_{23}CINO_{5}PPdS$ : C, 52.0; H, 3.5; N, 2.1%. Molar conductivity (S cm<sup>2</sup> mol<sup>-1</sup>): 150. IR (Nujol, cm<sup>-1</sup>): 8-mq 1585 w, 1510 vs, 826 s, 788 m, 769 m, 699 s; SPPh, 758 m, 752 m, 699 s, 690 s, 600 s [v(P-S)], 511 s;  $ClO_4^-$  1100 vs, 620 s; v(CO): 2115 vs (solid), 2118 (CH<sub>2</sub>Cl<sub>2</sub> solution). <sup>31</sup>P {<sup>1</sup>H} NMR:  $\delta$  45.65 (s). <sup>1</sup>H NMR:  $\delta$  8.81 (m, H1), 8.41 (d, H3, <sup>3</sup>J<sub>3-2</sub> = 7.93 Hz), 7-8 (m, H2, H4, H5, H6, SPPh<sub>3</sub>), 3.98 (s, -CH<sub>2</sub>-Pd). <sup>13</sup>C NMR:  $\delta$  151.09, 150.47, 142.59, 140.69, 130.14, 129.20, 128.91, 125.76, 122.34 (C<sub>9</sub>H<sub>6</sub>N), 36.57 (-CH<sub>2</sub>-Pd); 176.26 (CO).

#### $[Pd(8-mq)(CO)(SPMe_2Ph)]ClO_4$ (3b)

(a) Method 1. SPMe<sub>2</sub>Ph (0.104 g, 0.614 mmol) was added to a  $CH_2Cl_2$  suspension (20 cm<sup>3</sup>) of 1 (0.231 g,

0.614 mmol) and the mixture was stirred at room temperature for 5 min. After filtration of the suspended solid, cold Et<sub>2</sub>O (100 cm<sup>3</sup>,  $-10^{\circ}$ C) was added to the resulting solution giving rise to **3b** (0.110 g, 33% yield).

(b) Method 2. Carbon monoxide was bubbled through a suspension of  $[Pd(8-mq)(\mu-SPMe_2)]$ Ph)]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (0.150 g, 0.145 mmol) in  $2 \text{ cm}^3$  of CH<sub>2</sub>Cl<sub>2</sub> at  $-10^{\circ}$ C for 10 min. The resulting white solid was isolated by filtration and dried in vacuo, 3b (0.118 g, 75% yield). Found: C, 41.5; H, 3.7; N, 2.7. Calc. for C<sub>19</sub>H<sub>19</sub>ClNO<sub>5</sub>PPdS: C, 41.8; H, 3.5; N, 2.6%. Molar conductivity (S cm<sup>2</sup> mol<sup>-1</sup>): 172. IR (Nujol, cm<sup>-1</sup>): 8mg 1592 w, 1510 vs, 831 s, 789 m, 777 s, 691 s; SPMe<sub>2</sub>Ph 958 s, 929 vs, 754 s, 733 s, 563 s [v(P-S)];  $ClO_4^-$  1100 vs, 620 s; v(CO) 2113 vs (solid). <sup>31</sup>P {<sup>1</sup>H} NMR:  $\delta$  43.16 (s). <sup>1</sup>H NMR:  $\delta$  9.52 (m, H1), 8.41 (m, H3), 8.1-7.5 [m, H2, H4, H5, H6, C<sub>6</sub>H<sub>5</sub> (SPMe<sub>2</sub>Ph)], 3.92 (s, -CH<sub>2</sub>-Pd), 2.93 [d,  ${}^{2}J_{P-H} = 15$  Hz, Me  $(SPMe_2Ph)$ ]. The low solubility of **3b** prevented <sup>13</sup>C {<sup>1</sup>H} NMR measurements.

#### Crystallographic studies

Suitable single crystals for X-ray structure determination of  $[Pd(8-mq)(CO)(SPPh_3)]ClO_4$  (3a) were obtained by slow diffusion of a diethyl ether layer into a solution of 3a (8 mg) in CHCl<sub>3</sub> (4 cm<sup>3</sup>) at 5°C.

*Crystal data*. C<sub>29</sub>H<sub>23</sub>ClNO<sub>5</sub>PPdS, yellow, prismatic, M = 670.36, triclinic, space group P-1, a = 10.767(2), b = 10.843(1), c = 14.263(2) Å,  $\alpha = 85.31(1)$ ,  $\beta = 73.04(1)$ ,  $\gamma = 61.40(1)^{\circ}$ , V = 1395.1(3) Å<sup>3</sup>, Z = 2,  $D_c = 1.596$  g cm<sup>-3</sup>,  $\lambda = 0.71073$  Å, T = 200(2) K, crystal size =  $0.40 \times 0.34 \times 0.22$  mm,  $\mu$ (Mo- $K_z$ ) = 0.933 mm<sup>-1</sup>, F(000) = 676.

Data collection and processing. Siemens P4 automated four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device, graphite-monochomated Mo- $K_x$  radiation,  $\omega - \theta$  scan technique, 4650 independent reflections collected in two shells  $(2\theta < 40^\circ, 50^\circ; \theta \le h \le 12, -11 \le k \le 12, -15 \le l \le 16)$ , of which 4492 were used in all calculations, three check reflections measured at regular intervals showed no intensity decay. An empirical absorption correction based on psi scans was applied (transmission factors = 0.995 and 0.871).

Structure analysis and refinement. The position of the palladium atom was determined from the Patterson map. The remaining atoms were located in successive difference Fourier syntheses and refined by full-matrix least squares on  $F^2$ . All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were added at calculated positions with a common isotropic thermal parameter. At final convergence  $R[F \ge 4\sigma(F)] = 0.0302$ ,  $wR(F^2$ , all data) = 0.0772,  $S(F^2) = 1.029$  for 353 parameters,  $w^{-1} = [\sigma^2(F_0^2) + (0.0385 P)^2 + 1.53 P]$ , P = 1/3[max  $(F_0^2, 0) + 2F_e^2$ ], largest difference peak and hole = 0.996 and  $-0.560 e/Å^3$ . All calculations were I. Ara et al.

performed on a local area VAX cluster (VAX/VMS V5.5) with the Siemens SHELXTL PLUS and SHELXL 93 software packages [14,15].

#### **RESULTS AND DISCUSSION**

All the carbonylpalladium complexes described in this paper have been obtained as indicated in Scheme I.

# Synthesis and characterization of [Pd(8-mq) (OClO<sub>3</sub>)(CO)] (1)

When CO is bubbled through a suspension which contains the solvento species [Pd(8-mq)(OC- $Me_2$ <sub>x</sub> $ClO_4$  in  $CH_2Cl_2/Me_2CO$  (5:2) at -60 °C [Scheme I, (1)], the neutral monocarbonyl complex [Pd(8mq)(OClO<sub>3</sub>)(CO)] (1) precipitates. It is interesting to point out that, although CO is able to displace OClO<sub>3</sub> in other palladium complexes (M-OClO<sub>3</sub>) to produce the corresponding cationic carbonyl derivatives  $[M-CO]ClO_4$  [10a], in this case the neutral monocarbonyl complex is obtained instead of the cationic bis(carbonyl) complex  $[Pd(8-mq)(CO)_2]ClO_4$  which could be expected. Compound 1 is a stable solid at room temperature and can be stored at 5°C for long periods. Compound 1 is only slightly soluble in dichloromethane at room temperature and its solution decomposes very quickly rendering palladium metal. Decomposition can be partially prevented by working at low temperature; however, the solubility of this complex is very low under these conditions which prevents conductivity or NMR studies in solution.

The IR spectrum of 1 shows (see Experimental): (a) characteristic absorptions due to the OCIO<sub>3</sub><sup>-</sup> ligand [16]; (b) a strong absorption at 2140 cm<sup>-1</sup> due to v(CO), which suggests that only one isomer is formed in the reaction. Taking into account the trans disposition of the OClO3<sup>-</sup> anion to the C donor atom of the C,N-groups observed in complexes such as  $[Pd(C_6H_4-N = N-C_6H_5-C,N)(OClO_3)(SPPh_3)]$ [12]and [Pd(8-mq)(OClO<sub>3</sub>)(SPPh<sub>3</sub>)] [12,17], we think that 1 has the structure depicted in Scheme I, in concert with the value of v(CO) observed for a carbonyl group trans to a N donor atom in palladium carbonyl complexes [9,10b,18]. Since the carbonyl complex 1 is slightly stable in solution, we decided to explore its reactivity towards some neutral or anionic ligands (in a 1:1 molar ratio only) in order to establish whether the Pd-CO or Pd-OClO<sub>3</sub> is the more inert bond in the presence of nucleophiles.

Reactivity of  $[Pd(8-mq)(OCIO_3)(CO)]$  (1) towards anionic ligands. Synthesis of [Pd(8-mq)X(CO)] (X = Cl, Br, I)

In reactions between  $[Pd(8-mq)(OClO_3)(CO)]$  (1) and the halides  $(X^- = Cl^-, Br^-, I^-)$  in a 1:1 molar ratio the substitution of the perchlorate anion by the corresponding halides, which are better coordinating ligands, takes place giving rise to [Pd(8-mq)X(CO)][X = Cl (2a), Br (2b), I (2c)] with small impurities of



Scheme I.

the respective dinuclear compounds  $[Pd(8-mq)(\mu-X)]_2$ according to Scheme I (2). The latter seems to be formed by the intermolecular substitution of the CO by the halide. Pure samples of complexes **2a**, and **2c** have also been prepared by bubbling CO through suspensions of the dinuclear complexes  $[Pd(8-mq)(\mu-X)]_2(X = Cl, I)$  [Scheme I, (3)] [19]. Complexes **2a**, b, c are stable in the solid state at 5 °C for several months, but, at room temperature, their CH<sub>2</sub>Cl<sub>2</sub> solutions lose CO slowly, giving rise to the dinuclear derivatives  $[Pd(8-mq)(\mu-X)]_2$ .

Complexes 2a, b, c have been characterized by elemental analysis, IR and NMR (<sup>1</sup>H, <sup>13</sup>C) spectra. The IR spectra in CH<sub>2</sub>Cl<sub>2</sub> solution show only one absorption assignable to v(CO) at 2121 (2a), 2117 (2b) and 2110 (2c)  $cm^{-1}$ , respectively, indicating that only one isomer is present in each case. The sequence observed for v(CO) absorptions in 2a-2c is similar to that observed in the complexes  $[PdX_3(CO)]^-$  [4],  $[Pd(C_6H_4-C(R) = N-OH)X(CO)]$  [20] and [Pt(CO) $LX_2$ ] (X = Cl, Br, I; L = CO, py, aniline) [21] and can be explained by the different electronegativity of the halogens (Cl > Br > 1). Moreover, a higher v(CO)in  $[Pd(8-mq)(OClO_3)(CO)]$  (1) is also a consequence of the lower nucleophilic character of the OClO<sub>3</sub><sup>-</sup> ligand with respect to the  $X^-$  halides. The observed values of v(CO) in 2a-2c suggest that the CO ligand is *trans* to the N atom of the 8-mq group [18]. In addition, the v(Pd-Cl) for complex 2a is in the range observed in palladium chloro complexes with trans alkyl or phenyl groups [22]. The structure proposed for complexes 2a, b, c (Scheme I) is that observed in other complexes of stoichiometry [Pd(CN)XL] (C N = azobenzene-2, C, N; N, N-dimethylbenzylamine-2,*C*,*N*; 2-methoxy-3,*N*,*N*-dimethylaminopropyl; X =Cl, Br; L = py, PEt<sub>3</sub>, PPh<sub>3</sub>) obtained by cleavage of the halide-bridged system of the corresponding binuclear  $[Pd(C N)(\mu - X)]_2$  (X = Cl, Br) with neutral ligands (L) [23], and indicates that the substitution process [Scheme I (2)] takes place with stereoretention. The 'H NMR spectra of 2a, b, c show, in each case, six resonances corresponding to the six chemically inequivalent aromatic protons and a singlet resonance which is due to the methylene protons of the Pd––CH<sub>2</sub> group (see Experimental). The  $^{13}$ C <sup>1</sup>H} NMR spectra show the expected resonances for all the carbon atoms present in the different molecules, including the CO ligand. It is noteworthy that the moderate stability of these carbonyl complexes at a low temperature (-5 °C) allows a <sup>13</sup>C {<sup>1</sup>H} NMR study to be made, which is very unusual for Pd<sup>II</sup> carbonyl complexes [9].

# Reactions of $[Pd(8-mq)(OClO_3)(CO)]$ (1) with SPR<sub>3</sub>. Synthesis of $[Pd(8-mq)(CO)L]ClO_4$ [L = SPPh<sub>3</sub> (3a), SPMe<sub>2</sub>Ph (3b)]

 $[Pd(8-mq)(OClO_3)(CO)]$  (1) reacts with the neutral ligands SPPh<sub>3</sub> and SPMe<sub>2</sub>Ph (monodentate ligands

which are able to act as bridging ligands) in a 1:1 molar ratio giving rise to  $[Pd(8-mq)(CO)L]ClO_4$ [L = SPPh<sub>3</sub> (3a), SPMe<sub>2</sub>Ph (3b)], as is indicated in Scheme I (4). Both complexes are thermally stable and decompose between 130 and 140 °C. They have been isolated and fully characterized by elemental analysis, IR and NMR spectroscopy.

The structure of 3a and 3b (Scheme I) has been proposed on the basis of these data and confirmed by an X-ray study on 3a. The IR spectra of these complexes show: (a) absorptions due to the SPR<sub>3</sub> ligands. The absorption due to v(P-S) appears in both cases at lower frequencies than in the corresponding free ligand  $[\Delta v(P-S) = 36 \text{ cm}^{-1} (3a), 20 \text{ cm}^{-1} (3b)]$ . This small decrease indicates that, in both cases, the SPR<sub>3</sub> ligands act as terminal ligands [12]. (b) One absorption attributable to v(CO) at *ca* 2120 cm<sup>-1</sup> confirms the presence of the CO ligand in the complex. (c) Two absorptions at 1100 and 620 cm<sup>-1</sup>, which are typical of the uncoordinated  $ClO_4^{-}(Td)$  anion [16]. The <sup>1</sup>H NMR spectra of 3a, b show the resonances for all the groups that were expected to be present in the molecule, although the presence of phenyl groups in SPPh<sub>3</sub> and SPMe<sub>2</sub>Ph precludes any unambiguous assignment of the aromatic resonances. The  ${}^{31}P$  { ${}^{1}H$ } NMR spectra show only one singlet and the  ${}^{13}C {}^{1}H$ NMR spectrum of 3a shows the expected resonances for the cyclometallated group (8-mq) and the terminal CO ligand [9]. All these data confirm that the reactions take place with the substitution of the  $OClO_3^-$  ligand by L (L: SPPh<sub>3</sub>, SPMe<sub>2</sub>Ph) and that only one of the two possible isomers is formed in both cases. The molecular structure of 3a, which has been established by an X-ray diffraction study is discussed in detail below, indicates that the CO ligand is trans to the N atom (as in all the aforementioned complexes) of the 8-mg; i.e. that the substitution reaction of  $OClO_3^-$  by the L ligands on complex 1 [Scheme I (4)] occurred regiospecifically.

Complexes 3a and 3b can also be prepared by reacting CO with other starting materials. Thus, 3a is obtained when CO is bubbled through a dichloromethane solution of [Pd(8-mq)(OClO<sub>3</sub>)(SPPh<sub>3</sub>)] [Scheme I (5)]. Given the structure of the starting complex  $[Pd(8-mq)(OClO_3)(SPPh_3)]$  (which has been unequivocally established by a 'H-'H NOESY experiment [17]), in which the  $OClO_3^-$  group is *trans* to the  $\sigma$  Pd—C bond and the structure of **3a**, the substitution reaction of OClO<sub>3</sub><sup>-</sup> by CO takes place with isomerization and this isomerization process has to occur very quickly since, when the reaction is monitored in CH<sub>2</sub>Cl<sub>2</sub> solution by IR spectroscopy, no other isomers are detected. Isomerization processes have been observed previously, i.e. for trans-[PtX2(CO)L]  $(X = Cl, L = PBu_3, PEt_3, PMe_2Ph, PMePh_2, PPh_3,$ AsMePh<sub>2</sub>, AsPh<sub>3</sub>; X = Br,  $L = PMe_2Ph$ ) [24a], which isomerize to cis-[PtX<sub>2</sub>(CO)L], the trans to cis isomerization being dramatically catalyzed by carbon monoxide. The proposed mechanism for CO-catalyzed isomerizations is that of pseudorotation processes involving five-coordinate intermediates [24b]. Complex **3b** can also be prepared by carbonylation of the binuclear  $[Pd(8-mq)(\mu-SPMe_2Ph]_2$  [Scheme 1 (6)] which takes place with cleavage of the bridging system to produce only one isomer.

#### Molecular structure of [Pd(8-mq)(CO)(SPPh<sub>3</sub>)](CIO<sub>4</sub>) (3a)

The molecular structure of the cationic carbonyl palladium complex  $[Pd(8-mq)(CO)(SPPh_3)](ClO_4)$ (3a) has been determined by single crystal X-ray diffraction. A drawing of the structure is presented in Fig. 2 and relevant bond distances and bond angles are shown in Table 1.

As can be seen, the cation shows a slightly distorted square-planar geometry around the palladium centre with C(1) and C(2) atoms 0.154(6) Å and 0.126(5) Å away, respectively, from the best least-squares plane

C(28)

defined by the C(1), C(2), N(1), Pd(1) and S(1) atoms. The angle between the normal to this plane and the C(1)--O(1) vector is  $95.5(3)^{\circ}$  and the Pd--C-O angle is  $177.7(4)^{\circ}$ . The Pd—C(1) bond length [1.894(4) Å)] is within the range of distances observed in the neutral complex  $[Pd(\eta^3-C_4H_7)(SnCl_3)(CO)]$ [1.947(11) Å] [6] or the cationic [(phen)Pd(C(O)  $CH_{3}(CO)$ ]Ar'<sub>4</sub>B·CH<sub>2</sub>Cl<sub>2</sub> [1.922(11) Å] [9] and the anionic species  $[Pd(C_6H_3Me-2,NO_2-6)Cl_2(CO)]^{-1}$ [1.853(10) Å] [5], and is shorter than that observed in the cationic derivative [2-(CO)-2-(PPh<sub>3</sub>)-closo-2,1- $PdTeB_{10}H_9(PPh_3)$ ]<sup>+</sup> [2.003(9) Å] [7]. Bond distances and angles corresponding to the PdC<sub>10</sub>H<sub>8</sub>N metallocycle are similar to those observed in other complexes involving the 8-mq ligand [25]. The best leastsquares planes defined by the  $C_{10}H_8N$  ligand and the palladium coordination plane are not coplanar, but rather their dihedral angle is  $20.28(5)^{\circ}$ . The Pd—S(1) distance, 2.453(1) Å, is longer than that observed in

C(2)

C(3)

C(4)



0(1)

C(1)

Fig. 2. Molecular structure of the cation [Pd(8-mq)(CO)(SPPh<sub>3</sub>)]<sup>+</sup> showing the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table 1. Selected bond lengths (Å) and angles ( <sup>¬</sup> ) for complex [P	ed(8-mq)(CO)			
$(SPPh_3)]ClO_4$ (3a)				

Pd(1) - C(1) Pd(1) - N(1) C(1) - O(1)	1.894(4) 2.084(3) 1.123(4)	Pd(1)—C(2) Pd(1)—S(1)	2.062(3) 2.453(1)	
C(1)Pd(1)C N(1)Pd(1)S O(1)C(1)Pd	(2)87.7(2)(1)93.96(7)(1)177.7(4)	C(2)—Pd(1)—N C(1)—Pd(1)—S	I(1) 82.44(12) (1) 95.65(12)	

[Pd(az)(OClO<sub>3</sub>)(SPPh<sub>3</sub>)] (az: azobencene-2,C,N) [2.326(1) Å] [12] where the S atom is *trans* to a Pd—N bond, in accord with the greater *trans* influence of a C  $\sigma$ -bonded ligand than a Pd—N-bonded one.

# CONCLUSIONS

The of the neutral synthesis [Pd(8-mq)] $(OClO_3)(CO)$ ] (1), which is moderately stable, allows us to study its reaction with different neutral  $(SPR_3)$  or anionic (X<sup>-</sup>) ligands. In such processes, the Pd--CO bond is preserved and cationic and neutral carbonyl derivatives of palladium are obtained. However, the usual lability of the Pd-CO bond is also observed in these complexes since intermolecular substitution reactions involving CO displacement take place in their dichloromethane solutions. In spite of this fact  $^{13}C$  { $^{1}H$ } NMR data have been obtained for all sufficiently soluble complexes. The  $\delta C(CO)$  value is, in all cases, close to 177 ppm, a similar value to the corresponding resonance found in [(phen)Pd(C(O))] $CH_3$ )(CO)]Ar'<sub>4</sub>B·CH<sub>2</sub>Cl<sub>2</sub> [9].

Supplementary material—Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, H-atom coordinates and observed and calculated structure factors, have been deposited at the Cambridge Crystallographic Data Centre.

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