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Relevance to Synthetic Polynuclear Chemistry of Novel μ_3-Coordination Modes for the Anions $Ph_2PCHCOOC_2H_2^-$ and $Mo(CO)_3Cp^-$. Synthesis and X-ray Structure of $Pd(8\text{-mq})Br(Ph_2PCH_2COOC_2H_5)$, $\{[Pd(8\text{-mq})]_3(\mu_3\text{-}Ph_2PCHCOOC_2H_5)(\mu_3\text{-}OH)\}PF_6$, and $\{[Pd(8\text{-mq})]_3[\mu_3\text{-}Mo(CO)_3Cp](\mu_3\text{-}Cl)\}BF_4$

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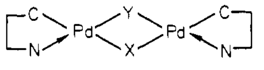
Abstract: The analogous role structurally played by the μ_2-organophosphorus $[Ph_2PCHC(O)OC_2H_5]$ and the μ_2-organometallic $[Mo(CO)_3Cp]$ bridges is illustrated by the molecular structure of the complexes $(8\text{-mq})Pd(\mu\text{-}Br)(\mu\text{-}Ph_2PCHC(O)OC_2H_5)Pd(8\text{-mq})$ (**1**) and $[(8\text{-mq})Pd]_2(\mu\text{-}Cl)(\mu\text{-}Mo(CO)_3C_p)$ (**3**) (8-mq-H = 8-methylquinoline). These bridges act in these molecules as three-electron donors. The analogy is further demonstrated by the reaction of **1** and **3** with Ag^+, leading respectively to the tri- and tetrametallic complexes $\{[Pd(8\text{-mq})]_3(\mu_3\text{-}Ph_2PCHCOOC_2H_5)(\mu_3\text{-}OH)\}PF_6$ (**2**) and $\{[Pd(8\text{-mq})]_3(\mu_3\text{-}Mo(CO)_3Cp)(\mu_3\text{-}Cl)\}BF_4$ (**5a**). The structure of both products was established by single-crystal X-ray analysis. Crystals of **2** belong to the space group $P2_1/n$, with a = 23.573 (9) Å, b = 15.789 (5) Å, c = 12.381 (4) Å, β = 100.21 (2)°, V = 4535 Å^3, and Z = 4. The structure has been refined to R = 0.073 and R_w = 0.087. The molecule consists of three Pd(8-mq) fragments held together by a μ_3-OH group and the Y ligand μ_3-bonded through the phosphorus, the α-carbon, and oxygen (C=O) atoms, respectively, to each of the palladium atoms. Complex **5a** crystallizes in the space group $C2/c$, with a = 23.877 (9) Å, b = 17.315 (6) Å, c = 19.142 (7) Å, β = 111.80 (2)°, V = 7348 Å^3, and Z = 8. The refinement of the structure has led to R = 0.047 and R_w = 0.063. The molecular structure shows three separated Pd centers bridged by a μ_3-Cl atom and a μ_3-Mo(CO)$_3$Cp moiety. The four metal atoms, the three carbon atoms of the carbonyls, and the bridging chloride define a distorted cubane structure for the inorganic core of **5a**. The unique bonding mode of Mo(CO)$_3$Cp involving the metal and all three carbonyls provides the first example where such a unit is coordinated to three metal centers. Complexes **2** and **5a** are envisaged as resulting from the addition of the unsaturated $[Pd(\overset{\frown}{CN})]^+$ fragment to **1** and **3**, respectively. In the first case, this is made possible by additional coordination through the ester function, and in the second case, by increased coordination from μ_2 to μ_3 of the bridging Cl and Mo(CO)$_3$Cp groups. This concept was verified by the rational quantitative synthesis of **5a** resulting from the addition of 1 equiv of $[Pd(8\text{-mq})(CH_3CN)_2]^+$ (**4**) to **3**. The analogy between the μ_3 organic fragment in **2** and μ_3-Mo(CO)$_3$Cp in **5a** allows their description as five-electron donors. The geometry of the cyclometalated 8-mq units of **2** and **5a** is discussed and compared to that of $Pd(8\text{-mq})Br(Ph_2PCH_2COOC_2H_5)$ (**6**). The molecular structure of the latter complex was established by X-ray diffraction: $C2/c$ with a = 18.691 (3) Å, b = 14.940 (1) Å, c = 17.722 (1) Å, β = 97.27 (2)°, V = 4909 Å^3, and Z = 8.

The research reported herein is a consequence of our preparative and structural results on a new class of organometallic dinuclear Pd(II) complexes containing two *different* bridging groups, X and Y.[2,3] The ancillary ligand on each palladium center is a three-electron donor cyclometalated $\overset{\frown}{CN}$ chelate (e.g., 8-methylquinoline, 8-mq; or dimethylbenzylamine, dmba) bonded to the metal through a hard-donor nitrogen and a softer σ-bonded carbon atom. Such a dissymmetric chelate may be expected to have a determining influence upon the structure and the reactivity of the bridging groups that are trans to it. In the complexes of type I, the bridging group X is an halide, while Y is either a functional carbanion or a carbonylmetalate anion. Thus, it was shown that the functional carbanions $[Ph_2PCHZ]^-$ (Z = CN, C(O)OC$_2$H$_5$) act as bridging ligands through the phosphorus and the carbon α to P in $[(\overset{\frown}{CN})Pd]_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PCHZ)$,[2] whereas the carbonylmetalates $[m]^-$ (e.g., m = η^5-C$_5$H$_5$Mo(CO)$_3$) bridge the palladium atoms through the metal and the carbonyl ligands in $[(\overset{\frown}{CN})Pd]_2(\mu\text{-}Cl)(\mu\text{-}m)$.[3]



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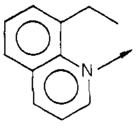
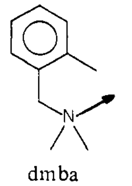


8-mq



dmba

X	Y	ref
Br	$Ph_2PCHC(O)OC_2H_5$ (1)	2
Br	Ph_2PCHCN	2
Cl	$Mo(CO)_3Cp$ (3)	this work
Br	$Ph_2PCHC(O)OC_2H_5$	2
Cl	$Ph_2PCHC(O)OC_2H_5$	2
Cl	Ph_2PCHCN	2
Cl	$Mo(CO)_3Cp$ (7)	3
Cl	$Co(CO)_4$	3
Cl	$Fe(CO)_3NO$	3

These complexes are characterized by a cis structure for the $\overset{\frown}{CN}$ chelates (revealed by both spectroscopy and X-ray diffraction) and by a trans position for the halide X with respect to the σ-bonded carbon atoms.[2,3] To our surprise, this arrangement was found with both types of group Y depicted above. The structural analogy thus revealed in these complexes between the behavior of an organic ligand and an organometallic fragment, led to the unusual description of the latter as a four-electron donor anionic ligand.[4] This was supported by the fact that in complex I the carbonylmetalate should contribute the same number of electrons as X$^-$ or as the bridging carbanion, by analogy with the

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[1] (a) Laboratorie de Chimie de Coordination. (b) Laboratoire de Cristallochimie.

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[4] The electron-count formalism used throughout this paper is the following: μ_2-X and μ_2-Y ligands in (I) are three-electron donors when considered neutral, four-electron donors when considered anionic.

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Table I. Crystal Data and Data Collection Parameters of 2, 5a, and 6

	2	5a	$6 \cdot H_2O$
formula	$C_{46}H_{41}F_6N_3O_3P_2Pd_3$	$C_{38}H_{29}BClF_4MoN_3O_3Pd_3$	$C_{26}H_{27}BrNO_3PPd$
M_r	1178.99	1113.07	618.79
crystal system	monoclinic	monoclinic	monoclinic
a, Å	23.573 (9)	23.877 (9)	18.691 (3)
b, Å	15.789 (5)	17.315 (6)	14.940 (1)
c, Å	12.381 (4)	19.142 (7)	17.722 (1)
β, deg	100.21 (2)	111.80 (2)	97.27 (2)
V, Å^3	4535	7348	4909
Z	4	8	8
ρ_{obsd}/ρ_{calcd}	1.73 ± 0.03/1.72	1.90 ± 0.03/2.01	1.65 ± 0.02/1.67
crystal dimension, mm	0.28 × 0.22 × 0.22	0.10 × 0.10 × 0.10	sphere $\phi = 0.20$
space group	$P2_1/n$	$C2/c$	$C2/c$
F_{000}	2332	4320	2480
diffractometer	Philips PW1100	Picker FACS 1	CAD4F
radiation	Cu Kα (graphite mono)	Mo Kα (graphite mono)	Cu Kα (Ni-filtered)
linear abs coeff, cm^{-1}	110.79	18.81	92.73
scan type	$\theta/2\theta$ flying step-scan	$\theta/2\theta$	$\theta/2\theta$
scan range, deg	$1.2 + 0.14 \tan \theta$	$1.2 + 0.29 \tan \theta$	$0.90 + 0.14 \tan \theta$
scan speed, deg min^{-1}	1.20	1	variable
θ limits, deg	4–55	1.5–30	4–65
no. of data collected	6083	7643	4390
unique data used	3179	5083	3354
R	0.073	0.047	0.041
R_w	0.087	0.063	0.061
std error observn of unit weight	1.69e	1.27e	1.15e
fudge factor	0.08	0.08	0.08

well-known 32-electron dinuclear $[(C^\frown N)Pd(\mu\text{-}X)]_2$ complexes.

The synthesis of these complexes was achieved by reacting the dinuclear $[(C^\frown N)Pd(\mu\text{-}X)]_2$ complexes[5,6] with 1 equiv of Y^-. Surprisingly, it was observed that *only one* bridging moiety Y could be incorporated in the complex. This was even more surprising in view of the trans influence that the σ-bonded carbon atom of each $C^\frown N$ chelate was expected to exert on X.[7,8]

We therefore decided to investigate the reactivity of this family of complexes toward halide abstractors, eg., $AgPF_6$. This has led to new and unexpected molecular rearrangements, accompanied by an increase in the nuclearity of the molecules, from Pd_2 to Pd_3 (in the case of the P–C bridge of **1**) and from Pd_2Mo to Pd_3Mo (in the case of the $CpMo(CO)_3$ bridge of **3**). These results are reported here.

Experimental Section

Details of the experimental procedure used throughout this work, including reagents and physical measurements, have been described in previous papers from our laboratory.[2,9]

A. Syntheses. The ligand $Ph_2PCH_2C(O)OC_2H_5$ (L^1) and the corresponding carbanion $[Ph_2PCHC(O)OC_2H_5]^-$ $(L^1)^-$ were synthesized by the methods described previously.[2,10] Solutions of $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ were prepared by Hg/Na reduction of THF solutions of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$.[11] Complexes $[Pd(8\text{-mq})X]_2$ (X = Cl, Br; 8-mq = 8-methylquinoline-*C,N*) were obtained by literature methods.[5]

The syntheses and properties of $\overline{Pd(8\text{-mq})(\mu\text{-Br})[\mu\text{-}Ph_2PCH(COOC_2H_5)]}Pd(8\text{-mq})$ (**1**) and of $Pd(8\text{-mq})Br[Ph_2PCH_2C(O)OC_2H_5]$ (**6**) have been reported previously.[2] Single crystals of **6** suitable for X-ray diffraction were obtained from an NMR solution (CD_2Cl_2) containing some water. The complex crystallized with one molecule of water.

{[Pd(8-mq)]$_3$(μ_3-Ph$_2$PCHCOOC$_2$H$_5$)(μ_3-OH)}PF$_6$ (2). A suspension of $AgPF_6$ (0.122 g, 0.48 mmol) in CH_2Cl_2 (5 mL) was added to a stirred solution of **1** (0.408 g, 0.48 mmol) in CH_2Cl_2 (25 mL). The solution immediately darkened and was rapidly filtered over a short layer of silica gel. Then pentane was added to the yellow solution, and after cooling at −20 °C, yellow crystals of **2** precipitated which were suitable for X-ray diffraction: 0.173 g, 42% (mp 174 °C dec; IR (Nujol) 1633 (s), 1595 (s), 1582 (sh) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ −0.69 (d, OH, $^3J(PH) = 2.6$ Hz), 1.30 (t, CH_3, $^3J = 7$ Hz), 2.56 and 3.29 (ABX pattern, CH^AH^B cis to P, $J(H^aH^B) = 15$ Hz, $^3J(PH^A) = 3.4$ Hz, $^3J(PH^B) = 3.8$ Hz), 2.74 (d, PCH, $^2J(PH) = 6.8$ Hz), 3.29 and 3.37 (AB pattern, $J(AB) = 14$ Hz), 3.89 and 4.08 (AB pattern, $J(AB) = 12$ Hz), 4.21 (q, CH_2CH_3, $^3J = 7$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 33.7. Anal. Calcd for $C_{46}H_{41}F_6N_3O_3P_2Pd_3$: C, 64.27; H, 4.81; N, 4.89. Found: C, 64.20; H, 4.92; N, 5.20.

[Pd(8-mq)]$_2$(μ-Cl)[μ-Mo(CO)$_3$(η^5-C$_5$H$_5$)] (3). A solution of $Na[Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ (0.1 M) in THF (30 mL) was added at room temperature to a stirred suspension of $[Pd(8\text{-mq})Cl]_2$ (1.704 g, 3.0 mmol) in THF (25 mL). The reaction occurs instantaneously and after 0.2-h stirring, a heavy red precipitate is obtained. It was filtered off, washed with water, THF, and *n*-pentane, and dried in vacuo; 1.78 g (yield 76 %) of compound **3** is thus obtained.

3 crystallized in a CH_2Cl_2/pentane solution as red microcrystals: mp 170 °C dec; IR (KBr) $\nu(CO)$ 1842 (m), 1760 (vs, br) cm^{-1}; far-IR bands (polyethylene disks) 267 (m, br), 249 (w), 232 (s), 214 (s), 205 (s) cm^{-1}. **3** is only slightly soluble in CH_2Cl_2, preventing any characterization in solution. Anal. Calcd for $C_{28}H_{21}ClMoN_2O_3Pd_2$: C, 43.24; H, 2.72; N, 3.60. Found: C 42.96; H, 3.12; N, 4.17.

[Pd(8-mq)(CH$_3$CN)$_2$]PF$_6$ (4). A suspension of $AgPF_6$ (0.253 g, 1 mmol) in CH_2Cl_2 (20 mL) was slowly added to a stirred suspension of $[Pd(8\text{-mq})Cl]_2$ (0.568 g, 1 mmol) in CH_2Cl_2 (20 mL) and CH_3CN (1 mL). After 0.1-h stirring the solution was filtered to remove AgCl and then concentrated. Addition of pentane afforded **4** as pale yellow crystals; 0.850 g, 90%. IR (nujol mull) $\nu(CN)$ 2323 (m), 2293 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.38 (3H, s, CH_3), 2.42 (3H, s, CH_3), 3.82 (2H, s, CH_2), 7.50–8.61 (6H, m, aromatic protons of 8-mq). Anal. Calcd for $C_{14}H_{14}F_6N_3PPd$: C, 35.34; H, 2.94; N, 8.83. Found: C 35.42; H, 3.14; N, 9.32.

{[Pd(8-mq)]$_3$[μ_3-Mo(CO)$_3$(η^5-C$_5$H$_5$)](μ_3-Cl)}BF$_4$ (5a). A suspension of $AgBF_4$ (0.065 g, 0.36 mmol) in CH_2Cl_2 (10 mL) was slowly added to a well-stirred suspension of compound **3** (0.285 g, 0.36 mmol) in CH_2Cl_2 (25 mL). The solution turned immediately red and a black precipitate formed. Sometimes a metallic mirror was observed in the Schlenk tube. The solution was filtered after 0.1-h stirring. Addition of *n*-hexane (50 mL) gave, after cooling at −20 °C, orange crystals; 0.250 g, 62%, mp 175 °C. Suitable single crystals for X-ray diffraction were grown from an acetone/diethyl ether solution at room temperature: IR (KBr) $\nu(CO)$ 1820 (w, sh), 1765 (vs, br), 1742 (vs, br), $\nu(BF)$ 1065 (s, br) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.80 (6H, s, 3 CH_2), 5.75 (5H, s, C_5H_5), 7.5–8.83 (18H, m, aromatic protons of 8-mq). Anal. Calcd for $C_{38}H_{29}BClF_4MoN_3O_3Pd_3$: C, 40.37; H, 2.58; N, 3.72. Found: C, 39.88; H, 1.99; N, 4.05.

{[Pd(8-mq)]$_3$[μ_3-Mo(CO)$_3$(η^5-C$_5$H$_5$)](μ_3-Cl)}PF$_6$ (5b). A solution of **4** (0.120 g, 0.25 mmol) in CH_2Cl_2 (20 mL) was added to a stirred suspension of compound **3** (0.200 g, 0.25 mmol) in CH_2Cl_2 (20 mL).

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Dissolution of 3 was complete after a few seconds. Addition of *n*-hexane to the clear red solution thus obtained afforded **5b** in almost quantitative yield mp 174 °C. IR (KBr) ν(CO) 1812 (w, sh), 1756 (vs, br); ν(PF) 840 (vs), δ(PF) 552 (vs) cm^{-1}; ^{1}H NMR data analogous to **5a**. Anal. Calcd for $C_{38}H_{29}ClF_6MoN_3O_3PPd_3$: C, 38.95; H, 2.48; N, 3.59. Found: C, 38.31; H, 2.21; N, 4.12.

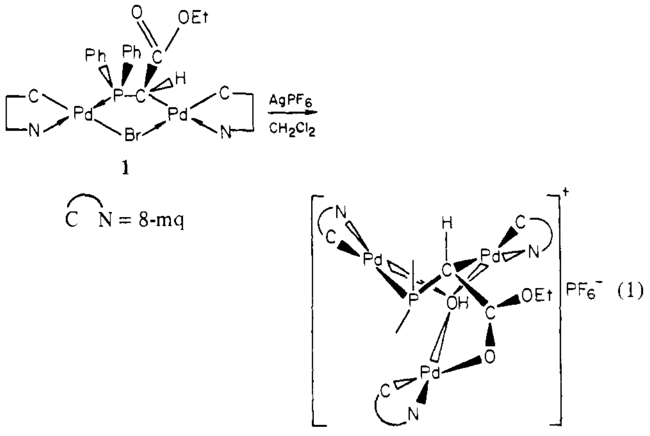
B. X-ray Data Collections and Structure Determination. Cell constants and other pertinent data are presented in Table I. Precise lattice parameters were obtained by standard Enraf-Nonius, Philips, and Picker least-squares methods using 25 carefully selected reflections. Intensity data were collected on automatic four-circle diffractometers. No intensity decay was observed during the data collection periods. For compound **2**, the raw step-scan data were converted to intensities using the Lehman–Larsen[12] algorithm on a PDP11/60 computer, and for all subsequent computations the Enraf–Nonius SDP/V16 package was used.[13]

Intensities were corrected for Lorentz and polarization factors; for **2** absorption corrections were applied by computed numerical integration[14] (transmission factors between 0.07 and 0.29).

The crystal structures were solved by using the MULTAN program[15] for **2** and the heavy-atom method for **5a** and **6** and refined by full matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located on difference maps and introduced by their computed coordinates in structure factor calculations but not refined (C–H: 0.95 Å, B_H = 8 Å^2 for **2**, 7 Å^2 for **5a** and **6**). The final difference maps showed no significant maxima. The refinement results are given in Table I. Anisotropic thermal parameters for all non-hydrogen atoms as well as a table listing the observed and calculated structure factor amplitutes of the reflections used in the refinement are available as supplementary material.[16]

Results and Discussion

Complexes with $[Ph_2PCH(O)OC_2H_5]^-$ (Y = CN, $COOC_2H_5$). We have previously shown that these anionic ligands react with dinuclear cyclometalated Pd(II) complexes of the type $[(\overset{\frown}{C\ N})Pd(\mu\text{-}X)]_2$ in a 1:1 stoichiometry to afford binuclear complexes of type I resulting from the replacement of one bridging X by the μ(*P,C*) fragment.[2] The X-ray structure of one complex of this type, $Pd(dmba)(\mu\text{-}Cl)[\mu\text{-}\overline{Ph_2PCH(COOC_2H_5)]Pd}(dmba)$, confirmed the indications obtained by IR and NMR spectroscopy that the ester function was not involved in the bonding to the metals. The same applies to the complexes where the $\overset{\frown}{C\ N}$ chelate is 8-mq instead of dmba and where the $-COOC_2H_5$ function is replaced by $-C{\equiv}N$. In these molecules, the functional carbanion therefore acts as a μ(*P,C*) bridging ligand. A chelate ($\overset{\frown}{P\ O}$) bonding mode for $[Ph_2PCHCOOC_2H_5]^-$ has also been encountered in $\overline{Pd(\overset{\frown}{C\ N})[Ph_2PCHC(O)}O\ C_2H_5]$.[2] A third coordination mode for this ligand has now been found in **2**, obtained from **1** by reaction with $AgPF_6$ in CH_2Cl_2 (eq 1) (details in the Experimental Section).



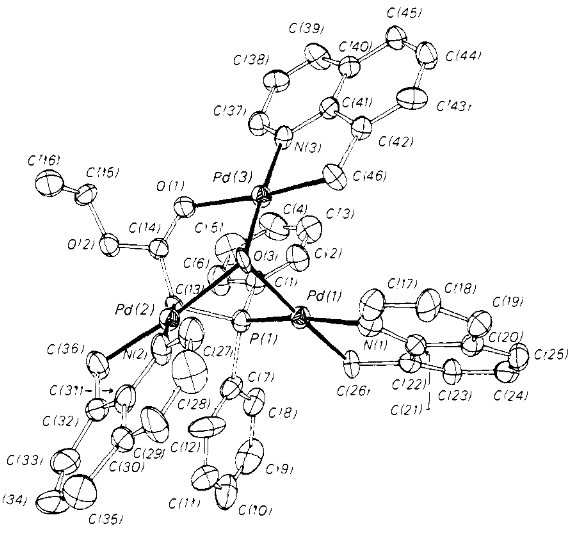


Figure 1. Structure of $\{[Pd(8\text{-}mq)]_3(\mu_3\text{-}OH)(\mu_3\text{-}Ph_2PCHCOOC_2H_5)\}PF_6$ (**2**).

This complex reaction deserves some comments. The determination of the structure of **2** by X-ray diffraction (Figure 1) allows the following hypothesis for its formation. Abstraction of the bridging halide in **1** induces such a destabilization of the molecule that partial fragmentation occurs. This would lead to a reactive solvated $[Pd(\overset{\frown}{C\ N})]^+$ unit[17] that could further add to the organic backbone of unreacted **1** through coordination of its free ester function. Upon coordination, the ν(C=O) frequency shifts from 1672 cm^{-1} in **1** to 1633 cm^{-1} in **2**. (Note, however, that this stretching mode contains a certain percentage of the ν(C–O) mode). This coordination is represented by the Pd(3)–O(1) bond in Figure 1. Furthermore, the crystal structure revealed that a bridging μ_3-OH group was present in **2**. Although the H atom could not be located by X-ray diffraction, both the observation of a doublet in the ^{1}H NMR at δ −0.69 (^3J(PH) = 2.6 Hz) (which disappears by exchange with D_2O) and the overall unipositive charge of the $[Pd_3]^+$ cation confirm the presence of the μ_3-OH group. The origin of this OH group is to be found either in traces of water in the solvents (we think this is unlikely) or in the water contained in the silica gel used for the filtration of the solution of **2** (see Experimental Section). The −OH group must be incorporated at a stage where the intermediate complex is quite reactive. Indeed, **1** alone does not exchange its μ-Br for a μ-OH under similar conditions. The latter point corroborates the previous observations[2,3] regarding the relative inertness of the bridging halide in complexes of type I. It stabilizes the whole molecule to a large extent, as also seen in the complexes where the other bridging group Y is a metal carbonyl fragment (see below). As soon as the bridging halide is removed by drastic reagents (*e.g.*, Ag^+), a dramatic molecular reorganization occurs.

When the reaction described in eq 1 was carried out with the related Pd(II) complexes containing the dmba $\overset{\frown}{C\ N}$ chelate, a greater instability of the products was noticed, leading to rapid decomposition. Furthermore, the presence of the 8-mq ligand appeared favorable in the attempts to grow single crystals for X-ray diffraction. The same observation was made in the systems where the bridging group is a metal carbonyl fragment instead of the functional carbanion. In the following section, we shall therefore only consider the complexes containing the 8-mq ligand.

The molecular structure of the cationic part of **2** is shown in Figure 1. Crystal data are given in Table I, the positional co-

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[16] See paragraph at the end of the paper regarding supplementary material.

[17] The other palladium containing fragment could be the known $\overline{Pd(\overset{\frown}{C\ N})[Ph_2PCHC(O)}OC_2H_5]$ complex.[2] However, it was not clearly identified in the reactive mixture.

Table II. Positional Parameters and Their Estimated Standard Deviations for **2**

atom	x	y	z	B, Å$^{2\,a}$
Pd(1)	0.32199 (6)	0.25965 (8)	0.1820 (1)	5.36 (3)
Pd(2)	0.37208 (6)	0.33650 (8)	0.4253 (1)	5.36 (3)
Pd(3)	0.40904 (6)	0.39845 (8)	0.1487 (1)	5.17 (3)
O(3)	0.4096 (6)	0.3048 (6)	0.2743 (8)	6.0 (3)
P(1)	0.2773 (2)	0.3752 (3)	0.2280 (4)	5.4 (1)
C(1)	0.2103 (8)	0.352 (1)	0.279 (2)	6.7 (5)
C(2)	0.1575 (9)	0.362 (1)	0.215 (2)	8.3 (6)
C(3)	0.1073 (9)	0.329 (2)	0.260 (3)	11.3 (8)
C(4)	0.116 (1)	0.288 (2)	0.357 (2)	11.7 (8)
C(5)	0.164 (1)	0.283 (2)	0.410 (2)	11.2 (8)
C(6)	0.216 (1)	0.308 (2)	0.380 (3)	11.8 (8)
C(7)	0.2566 (9)	0.456 (1)	0.122 (1)	6.2 (5)
C(8)	0.261 (1)	0.445 (1)	0.021 (1)	7.8 (6)
C(9)	0.249 (1)	0.501 (2)	−0.063 (2)	8.9 (6)
C(10)	0.228 (1)	0.580 (2)	−0.038 (2)	11.2 (8)
C(11)	0.223 (1)	0.597 (2)	0.069 (3)	12.2 (9)
C(12)	0.236 (1)	0.532 (2)	0.155 (2)	9.7 (7)
C(13)	0.3175 (8)	0.428 (1)	0.347 (1)	5.2 (4)
C(14)	0.3571 (8)	0.497 (1)	0.325 (1)	5.6 (4)
O(1)	0.3876 (5)	0.4996 (7)	0.2537 (9)	6.2 (3)
O(2)	0.3593 (5)	0.5582 (7)	0.3977 (9)	6.4 (3)
C(15)	0.4011 (9)	0.622 (1)	0.399 (2)	7.1 (5)
C(16)	0.451 (1)	0.608 (2)	0.484 (2)	10.3 (8)
N(1)	0.3519 (7)	0.1402 (9)	0.129 (1)	6.2 (4)
C(17)	0.4024 (9)	0.110 (1)	0.157 (2)	7.4 (5)
C(18)	0.419 (1)	0.035 (1)	0.106 (2)	7.7 (6)
C(19)	0.381 (1)	0.000 (1)	0.020 (2)	8.1 (6)
C(20)	0.3254 (8)	0.035 (1)	−0.011 (1)	5.6 (4)
C(21)	0.3125 (8)	0.105 (1)	0.052 (1)	5.7 (4)
C(22)	0.2578 (8)	0.143 (1)	0.023 (1)	6.2 (5)
C(23)	0.2213 (9)	0.121 (1)	−0.066 (2)	7.6 (5)
C(24)	0.237 (1)	0.048 (2)	−0.126 (2)	8.8 (6)
C(25)	0.2862 (8)	0.009 (1)	−0.104 (2)	7.5 (5)
C(26)	0.2458 (8)	0.217 (1)	0.096 (1)	6.0 (4)
N(2)	0.4156 (8)	0.2390 (9)	0.515 (1)	6.8 (4)
C(27)	0.453 (1)	0.184 (1)	0.490 (2)	8.2 (6)
C(28)	0.469 (1)	0.109 (1)	0.554 (2)	11.4 (8)
C(29)	0.448 (1)	0.093 (1)	0.642 (2)	9.9 (7)
C(30)	0.409 (1)	0.148 (1)	0.672 (1)	8.3 (6)
C(31)	0.3937 (9)	0.225 (1)	0.610 (1)	6.6 (5)
C(32)	0.3563 (8)	0.285 (1)	0.634 (1)	6.1 (4)
C(33)	0.331 (1)	0.267 (2)	0.723 (2)	9.8 (7)
C(34)	0.348 (1)	0.197 (2)	0.795 (2)	11.2 (8)
C(35)	0.384 (2)	0.143 (2)	0.770 (2)	13 (1)
C(36)	0.346 (1)	0.372 (1)	0.569 (2)	7.8 (6)
N(3)	0.4131 (6)	0.4767 (8)	0.024 (1)	5.2 (3)
C(37)	0.3993 (9)	0.555 (1)	0.017 (2)	6.5 (5)
C(38)	0.406 (1)	0.609 (1)	−0.077 (2)	7.7 (5)
C(39)	0.428 (1)	0.574 (1)	−0.154 (1)	7.8 (5)
C(40)	0.4437 (8)	0.488 (1)	−0.154 (1)	6.3 (5)
C(41)	0.4367 (8)	0.443 (1)	−0.061 (1)	5.3 (4)
C(42)	0.4482 (8)	0.353 (1)	−0.052 (1)	5.6 (4)
C(43)	0.4738 (8)	0.312 (1)	−0.134 (2)	7.9 (6)
C(44)	0.480 (1)	0.362 (1)	−0.222 (1)	7.3 (5)
C(45)	0.4712 (8)	0.446 (1)	−0.232 (1)	6.5 (6)
C(46)	0.4373 (9)	0.312 (1)	0.051 (1)	6.6 (5)
P(2)	0.5835 (3)	0.1653 (4)	0.2795 (6)	8.8 (2)
F(1)	0.5306 (9)	0.230 (1)	0.280 (1)	14.6 (6)
F(2)	0.537 (1)	0.101 (1)	0.277 (3)	24 (1)
F(3)	0.6268 (8)	0.096 (1)	0.275 (2)	16.8 (7)
F(4)	0.627 (1)	0.231 (2)	0.271 (3)	22 (1)
F(5)	0.565 (1)	0.174 (2)	0.153 (2)	20.0 (8)
F(6)	0.599 (1)	0.159 (2)	0.398 (2)	22.5 (9)
H2	0.1508	0.3881	0.1440	8*
H3	0.0680	0.3415	0.2170	8*
H4	0.0821	0.2653	0.3784	8*
H5	0.1678	0.2624	0.4902	8*
H6	0.2543	0.2965	0.4274	8*
H8	0.2734	0.3898	−0.0006	8*
H9	0.2567	0.4954	−0.1367	8*
H10	0.2124	0.6242	−0.0860	8*
H11	0.2097	0.6559	0.0943	8*
H12	0.2289	0.5447	0.2331	8*
H13	0.3115	0.4175	0.4213	8*
H15	0.3846	0.6782	0.4161	8*
H15	0.4120	0.6299	0.3291	8*
H16	0.4795	0.6475	0.4865	8*
H16	0.4394	0.6002	0.5531	8*
H16	0.4668	0.5518	0.4660	8*
H17	0.4308	0.1388	0.2120	8*
H18	0.4570	0.0075	0.1339	8*
H19	0.3937	−0.0467	−0.0185	8*
H23	0.1847	0.1542	−0.0909	8*
H24	0.2085	0.0266	−0.1883	8*
H25	0.2967	−0.0379	−0.1491	8*
H26	0.2213	0.1969	0.1455	8*
H26	0.2255	0.2614	0.0528	8*
H27	0.4654	0.1924	0.4187	8*
H28	0.4995	0.0710	0.5258	8*
H29	0.4631	0.0449	0.6871	8*
H33	0.3030	0.3131	0.7424	8*
H34	0.3293	0.1879	0.8580	8*
H35	0.3978	0.0950	0.8165	8*
H36	0.3698	0.4148	0.6059	8*
H36	0.3071	0.3886	0.5572	8*
H37	0.3821	0.5817	0.0767	8*
H38	0.3931	0.6668	−0.0811	8*
H39	0.4326	0.6107	−0.2158	8*
H43	0.4840	0.2513	−0.1251	8*
H44	0.4961	0.3315	−0.2813	8*
H45	0.4805	0.4784	−0.2957	8*
H46	0.4718	0.2864	0.0920	8*
H46	0.4088	0.2680	0.0361	8*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab\cos\gamma B_{1,2} + ac\cos\beta B_{1,3} + bc\cos\alpha B_{2,3}]$.

ordinates in Table II, the interatomic distances and angles in Table III, and least-squares planes in Table IV. The PF_6^- counterion is not represented and has a distorted octahedral geometry[18] (see Table III).

The structure of the cation can be analyzed in the following fragments: (i) three Pd(8-mq) units, (ii) the bridging μ_3-(Ph_2*P*CHC*O*OC_2H_5) ligand P, C, and O bonded to Pd(1), Pd(2) and Pd(3), respectively, (iii) the bridging μ_3-OH group capping the three palladium atoms.

(i) The three palladium have a square-planar coordination, as expected for d^8 Pd(II) ions. But their coordination planes are slightly distorted as indicated in Table IV. As deduced from the large Pd···Pd separations [Pd(1)–Pd(3), 3.080 (1); Pd(1)–Pd(2), 3.268 (1); Pd(2)-Pd(3), 3.808 (1) Å] no metal–metal interaction is to be found in this complex. In the ^{1}H NMR, each 8-mq is characterized by a different chemical shift for the CH_2 protons. Two CH_2 groups [C(26) and C(36)] are trans with respect to *O*(3), whereas the third one [C(46)] is trans to O(1).

In agreement with the absence of any symmetry element in **2**, an ABX pattern is observed for the protons at C(26) with $J(H^AH^B)$ = 15 Hz, $^3J(PH^A)$ = 3.4 Hz, and $^3J(PH^B)$ = 3.8 Hz, whereas an AB pattern is found for the protons at C(36) and C(46) (see Experimental Section).[19] The observation of the single

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[18] For comparison, a normal O_h symmetry for PF_6^- has been found in, *e.g.*: Adams, H.; Bailey, N. A.; Briggs, T. N.; Mc Cleverty, J. A.; Colquhoun, H. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1521.

[19] This contrasts with the isochronous CH_2 protons of the 8-mq ligand in the bimetallic complex Pd(dmba)(μ-Br)[μ-$Ph_2PCH(COOC_2H_5)$]Pd(8-mq).[2] Likewise in **1**, the 8-mq CH_2 group cis to $C(COOC_2H_5)$ gives rise to a singlet.[2] Such behavior either indicates that in solution at room temperature a dynamic process occurs on the NMR time scale which creates an average plane of symmetry for these CH_2 groups or results from accidental degeneracy of the H resonances.

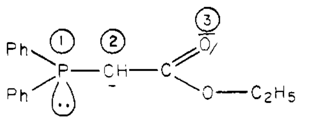
Table III. Selected Interatomic Distances (Å) and Angles (deg) in $\{[Pd(8\text{-}mq)]_3(\mu_3\text{-}OH)(\mu_3\text{-}Ph_2PCHCOOC_2H_5)\}PF_6$ (**2**)

Pd(1)–P(1)	2.231 (4)	N(1)–Pd(1)–O(3)	96.3 (4)
Pd(1)–O(3)	2.28 (1)	N(1)–Pd(1)–P(1)	171.0 (4)
Pd(1)–N(1)	2.15 (1)	N(1)–Pd(1)–C(26)	81.6 (5)
Pd(1)–C(26)	2.03 (1)	O(3)–Pd(1)–P(1)	92.4 (3)
		O(3)–Pd(1)–C(26)	177.6 (4)
Pd(2)–O(3)	2.261 (8)	P(1)–Pd(1)–C(26)	89.5 (4)
Pd(2)–C(13)	2.06 (1)		
Pd(2)–N(2)	2.06 (1)	N(2)–Pd(2)–O(3)	93.0 (5)
Pd(2)–C(36)	2.06 (2)	N(2)–Pd(2)–C(13)	170.7 (6)
		N(2)–Pd(2)–C(36)	86.2 (6)
Pd(3)–O(1)	2.17 (1)	O(3)–Pd(2)–C(13)	93.9 (4)
Pd(3)–O(3)	2.144 (9)	O(3)–Pd(2)–C(36)	174.0 (6)
Pd(3)–N(3)	1.99 (1)	C(13)–Pd(2)–C(36)	87.4 (6)
Pd(3)–C(46)	2.01 (1)		
		N(3)–Pd(3)–O(1)	93.2 (4)
P(1)–C(1)	1.84 (2)	N(3)–Pd(3)–O(3)	173.9 (4)
P(1)–C(7)	1.82 (1)	N(3)–Pd(3)–C(46)	83.7 (6)
P(1)–C(13)	1.81 (1)	O(1)–Pd(3)–O(3)	92.6 (3)
C(13)–C(14)	1.48 (2)	O(1)–Pd(3)–C(46)	173.6 (5)
C(14)–O(1)	1.23 (2)	O(3)–Pd(3)–C(46)	90.2 (5)
C(14)–O(2)	1.31 (2)	Pd(1)–O(3)–Pd(2)	91.8 (4)
O(2)–C(15)	1.41 (2)	Pd(1)–O(3)–Pd(3)	87.9 (3)
C(15)–C(16)	1.45 (3)	Pd(2)–O(3)–Pd(3)	119.6 (4)
mean C⩦C in phenyl rings	1.373 (8)	C(1)–P(1)–C(7)	104.2 (8)
		C(1)–P(1)–C(13)	99.8 (7)
Pd(1)···Pd(2)	3.268	C(7)–P(1)–C(13)	107.2 (6)
Pd(1)···Pd(3)	3.080		
Pd(2)···Pd(3)	3.808	P(1)–C(13)–C(14)	116.5 (9)
P(2)–F(1)	1.61 (1)	C(13)–C(14)–O(1)	128 (1)
P(2)–F(2)	1.49 (2)	C(13)–C(14)–O(2)	111 (1)
P(2)–F(3)	1.50 (1)	C(14)–O(2)–C(15)	118 (1)
P(2)–F(4)	1.47 (2)	O(2)–C(15)–C(16)	111 (1)
P(2)–F(5)	1.55 (2)		
P(2)–F(6)	1.45 (2)		

resonance at 33.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum of **2** excludes the presence of different isomers. This value is intermediate between that found in $Pd(8\text{-}mq)[Pd_2PCHC(O)OC_2H_5]$ (17 ppm) and that in **1** (39.5 ppm) where the phosphorus atoms were part of five-membered rings.[2,20]

Details of the structural parameters for each Pd(8-mq) moiety are given below and compared in Table XI with the corresponding data for the other structures described in this paper.

(ii) The functional carbanion ligand $[Ph_2PCHC(O)OC_2H_5]^-$ exhibits in **2** an unprecedented μ_3 coordination mode. Indeed, it is P bonded to Pd(1), C bonded to Pd(2), and also O (>C = O) bonded to Pd(3). The three functionalities potentially available for coordination: the phosphorus lone pair, the carbanionic carbon, and the ester function, are now all involved in bonding to the metals.



Whereas functionalities one and two are used in molecules like **1** to bridge the two metal ions,[2] functionalities one and three participate to the bonding in a chelate manner in complexes like Pd(C⌒N)$[Ph_2PCHC(O)OC_2H_5]$.[2] With the neutral phosphines Ph_2PCH_2Z (Z = $COOC_2H_5$, CN), function one only (monodentate ligand), or one and three, (chelating or bridging ligand) can be used for coordination to a metal center.[10] The most significant change on going from $[Pd(dmba)]_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PCHC(O)OC_2H_5)^2$ to **2** is the expected lengthening [from 1.15 (2) Å to 1.23 (2) Å] of the C(14)–O(1) bond upon coordination of O(1) to Pd(3) (Table XII).

For structural comparison, we have determined the crystal structure of **6** where the phosphine acts as a phosphorus-bound

Table IV. Least-Squares Planes for $\{[Pd(8\text{-}mq)]_3(\mu_3\text{-}OH)(\mu_3\text{-}Ph_2PCHCOOC_2H_5)\}PF_6$ (2)

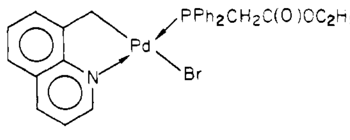
plane no.	atoms	distance from plane, Å	plane no.	atoms	distance from plane, Å
1[b]	Pd(1)	0.001 (1)	5[b]	Pd(3)	0.002 (1)
	N(1)	−0.056 (14)		N(3)	−0.031 (14)
	C(26)	0.036 (17)		C(46)	−0.148 (20)
	O(3)	0.008 (10)		O(3)	−0.022 (13)
	P(1)	−0.005 (5)		O(1)	−0.052 (12)
2	Pd(1)	0.000 (1)	6	Pd(3)	0.000 (1)
	N(1)	0.000 (14)		N(3)	0.000 (14)
	C(26)	0.000 (17)		C(46)	0.000 (20)
	C(21)[a]	0.256 (16)		C(41)[a]	−0.132 (17)
	C(22)[a]	0.375 (18)		C(42)[a]	−0.075 (18)
3[b]	Pd(2)	0.000 (1)	7	C(13)	−0.005 (16)
	N(2)	0.106 (16)		C(14)	0.018 (18)
	C(36)	−0.180 (23)		O(1)	−0.003 (12)
	O(3)	−0.035 (12)		O(2)	−0.003 (12)
	C(13)	0.116 (17)		P(1)[a]	0.931 (5)
4	Pd(2)	0.000 (1)			
	N(2)	0.000 (17)			
	C(36)	0.000 (24)			
	C(31)[a]	0.427 (20)			
	C(32)[a]	0.533 (19)			

plane	angle, deg	plane	angle, deg
Dihedral Angles between the Planes			
1–2	1.9	3–4	6.0
1–3	107.6	3–5	30.0
1–5	95.6	5–6	4.3

plane	*A*	*B*	*C*	*D*
Equations of the Planes of the Form $Ax + By + Cz - D = 0$[c]				
1	0.3276	0.4580	−0.8264	2.3997
2	0.3561	0.4398	−0.8245	2.5353
3	−0.7111	−0.6472	−0.2749	−10.4357
4	−0.7794	−0.5829	−0.2299	−10.3965
5	−0.9203	−0.1799	−0.3474	−10.4254
6	−0.8892	−0.2254	−0.3982	−10.4229
7	−0.6489	0.4609	−0.6054	−3.7994

[a] This atom was not used in defining the plane. [b] The χ^2 values of these planes range from 22 to 157. [c] Orthogonalized coordinates according to: Blow, D. M. *Acta Crystallogr.* 1960, *13*, 168.

monodentate ligand. Although this bonding mode has been previously found in a number of complexes with this phosphine,[2,10] none of them had been structurally investigated by X-ray diffraction.[21]



6

Complex **6** was prepared by reaction of 2 equiv of $Ph_2PCH_2C(O)OC_2H_5$ with $[(8\text{-}mq)Pd(\mu\text{-}Br)]_2$. Its molecular structure is shown in Figure 2. Crystal data are given in Table I, the positional coordinates in Table V, the interatomic distances and angles in Table VI, and least-squares planes in Table VII. The X-ray structure of this square planar complex confirms our previous structural hypothesis, based on IR and NMR spectroscopy.[2] Indeed, the phosphorus is trans to the nitrogen, the bromide trans to the σ-bonded carbon atom, and no interaction between the metal and the ester function is to be found [Pd···O(1) = 3.899 Å]. The structural parameters concerning the Pd(8-mq) moiety are normal and are compared in Table XI with the data for the other known structures containing this fragment. The Pd–P

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(20) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(21) By contrast, coordination of function one alone has never been observed in stable complexes of $[Ph_2PCHZ]^-$, amenable for X-ray diffraction studies.

Table V. Positional Parameters and Their Estimated Standard Deviations for **6**

atom	x	y	z	B, Å$^{2\,a}$
Pd	0.82763 (2)	0.19363 (3)	0.33524 (2)	3.627 (8)
Br	0.84802 (4)	0.02628 (4)	0.31347 (4)	4.76 (1)
P	0.79179 (8)	0.22087 (9)	0.21242 (8)	3.66 (3)
C(1)	0.6971 (3)	0.1914 (4)	0.1888 (3)	3.9 (1)
C(2)	0.6433 (4)	0.2564 (5)	0.1810 (4)	5.0 (1)
C(3)	0.5715 (4)	0.2309 (6)	0.1709 (4)	6.4 (2)
C(4)	0.5536 (4)	0.1420 (6)	0.1712 (5)	6.7 (2)
C(5)	0.6056 (4)	0.0792 (5)	0.1779 (4)	6.1 (2)
C(6)	0.6786 (3)	0.1013 (4)	0.1874 (4)	4.8 (1)
C(7)	0.8405 (3)	0.1650 (4)	0.1433 (3)	3.8 (1)
C(8)	0.9128 (4)	0.1507 (5)	0.1617 (3)	4.9 (1)
C(9)	0.9550 (4)	0.1243 (5)	0.1074 (4)	5.5 (2)
C(10)	0.9240 (4)	0.1095 (5)	0.0336 (4)	5.7 (2)
C(11)	0.8507 (4)	0.1220 (5)	0.0137 (4)	5.6 (2)
C(12)	0.8092 (4)	0.1499 (5)	0.0685 (3)	4.8 (1)
C(13)	0.7940 (3)	0.3361 (4)	0.1769 (3)	4.4 (1)
O(1)	0.9120 (3)	0.3884 (5)	0.2295 (3)	9.4 (2)
O(2)	0.8875 (3)	0.3690 (4)	0.1051 (3)	6.8 (1)
C(14)	0.8716 (4)	0.3684 (4)	0.1760 (4)	5.8 (2)
C(15)	0.9611 (5)	0.3968 (7)	0.0973 (6)	10.5 (3)
C(16)	0.9830 (6)	0.3716 (9)	0.0342 (8)	13.7 (4)
N	0.8554 (3)	0.1875 (3)	0.4533 (3)	4.4 (1)
C(17)	0.8077 (4)	0.3242 (4)	0.3595 (4)	4.9 (1)
C(18)	0.8154 (3)	0.3358 (4)	0.4429 (4)	4.7 (1)
C(19)	0.7981 (4)	0.4142 (5)	0.4768 (4)	6.1 (2)
C(20)	0.8099 (5)	0.4245 (6)	0.5574 (4)	7.2 (2)
C(21)	0.8377 (4)	0.3521 (6)	0.6035 (4)	6.5 (2)
C(22)	0.8548 (4)	0.2740 (5)	0.5700 (4)	5.3 (1)
C(23)	0.8834 (4)	0.1965 (5)	0.6124 (4)	5.7 (2)
C(24)	0.8951 (4)	0.1225 (6)	0.5741 (4)	6.3 (2)
C(25)	0.8816 (4)	0.1191 (5)	0.4955 (3)	5.1 (2)
C(26)	0.8434 (3)	0.2644 (4)	0.4903 (3)	4.5 (1)
O(3)	0.500	0.4297 (5)	0.250	7.5 (2)
HC2	0.6568	0.3197	0.1833	6*
HC3	0.5335	0.2768	0.1649	6*
HC4	0.5023	0.1248	0.1649	6*
HC5	0.5916	0.0164	0.1764	6*
HC6	0.7165	0.0561	0.1913	6*
HC8	0.9345	0.1603	0.2128	6*
HC9	1.0062	0.1156	0.1209	6*
HC10	0.9536	0.0880	−0.0029	6*
HC11	0.8298	0.1097	−0.0375	6*
HC12	0.7570	0.1582	0.0556	6*
HC25	0.8919	0.0645	0.4683	6*
HC24	0.9118	0.0692	0.6022	6*
HC23	0.8944	0.2004	0.6673	6*
HC21	0.8451	0.3593	0.6583	6*
HC20	0.7967	0.4805	0.5817	6*
HC19	0.7773	0.4646	0.4454	6*
H1C17	0.8418	0.3621	0.3376	6*
H2C17	0.7605	0.3406	0.3362	6*
H1C13	0.7701	0.3744	0.2102	6*
H2C13	0.7683	0.3393	0.1276	6*
H1C15	0.9967	0.3623	0.1361	6*
H2C15	0.9712	0.4577	0.1107	6*
H1C16	1.0278	0.3922	0.0186	6*
H2C16	0.9729	0.3140	0.0140	6*
H3C16	0.9474	0.4094	−0.0113	6*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab\cos\gamma B_{1,2} + ac\cos\beta B_{1,3} + bc\cos\alpha B_{2,3}]$.

distance of 2.232 (1) Å is normal for such a bond,[22] and the Pd–Br distance of 2.566 (1) Å is typical for a bromide trans to a ligand of high trans influence.[7] Selected structural data for the Pd($Ph_2PCH_2COOC_2H_5$) moiety are compared in Table XII with the related data taken from this and previous work.

(iii) The bridging μ_3-OH$^-$ group acts here as a six-electron donor anionic ligand. It interacts with the metals via two dative bonds, one being O(3)–Pd(2), and a covalent bond. We have no criteria

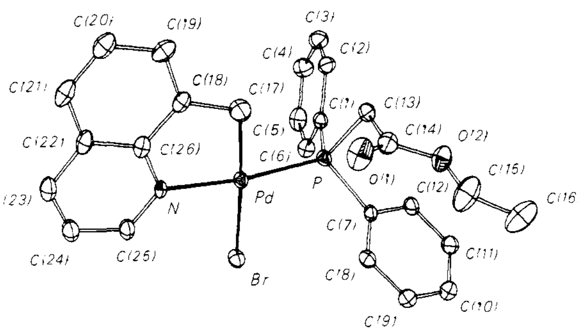

Figure 2. Structure of $Pd(8\text{-}mq)Br(Ph_2PCH_2COOC_2H_5)$ (**6**).

Table VI. Selected Interatomic Distances (Å) and Angles (deg) in $Pd(8\text{-}mq)Br(Ph_2PCH_2COOC_2H_5)$ (**6**)

Pd–P	2.232 (1)	Br–Pd–P	93.61 (4)
Pd–Br	2.566 (1)	Br–Pd–C(17)	175.6 (2)
Pd–N	2.094 (5)	Br–Pd–N	94.8 (1)
Pd–C(17)	2.042 (6)	P–Pd–C(17)	89.5 (2)
Pd···O(1)	3.90	P–Pd–N	171.3 (1)
		N–Pd–C(17)	81.9 (2)
P–C(1)	1.820 (6)	C(1)–P–C(7)	106.8 (2)
P–C(7)	1.819 (6)	C(1)–P–C(13)	102.2 (2)
P–C(13)	1.836 (6)	C(7)–P–C(13)	99.4 (2)
C(13)–C(14)	1.530 (9)	P–C(13)–C(14)	111.2 (4)
C(14)–O(1)	1.173 (9)	C(13)–C(14)–O(1)	125.8 (7)
C(14)–O(2)	1.328 (8)	C(13)–C(14)–O(2)	109.7 (6)
O(2)–C(15)	1.46 (1)	C(14)–O(2)–C(15)	114.6 (7)
C(15)–C(16)	1.29 (1)	O(2)–C(15)–C(16)	113 (1)
mean C$\overset{...}{-}$C in phenyl rings	1.380 (3)		

Table VII. Least-Squares Planes for $Pd(8\text{-}mq)Br(Ph_2PCH_2COOC_2H_5)$ 6

plane no.	atoms	distance from plane, Å	plane no.	atoms	distance from plane, Å
1	Pd	0.002 (0)	3	Pd	0.000 (0)
	N	−0.001 (1)		C(17)	0.000 (7)
	C(17)	−0.057 (5)		N	0.000 (5)
	Br	−0.103 (7)		C(26)^a	−0.097 (6)
	P	−0.005 (2)		C(18)^a	−0.158 (6)
2	N	−0.014 (5)	4	C(13)	−0.001 (6)
	C(18)	0.022 (6)		C(14)	0.006 (7)
	C(19)	−0.018 (8)		O(1)	−0.002 (7)
	C(20)	−0.018 (9)		O(2)	−0.001 (5)
	C(21)	−0.019 (7)			
	C(22)	0.017 (7)			
	C(23)	0.016 (8)			
	C(24)	−0.008 (8)			
	C(25)	−0.011 (7)			
	C(26)	0.023 (6)			
	C(17)^a	0.096 (7)			
	Pd^a	−0.097 (0)			

plane	angle, deg	plane	angle, deg
Dihedral Angles between the Planes			
1–2	1.2	2–3	7.7
1–3	8.8		

plane	A	B	C	D
Equations of the Planes of the form $Ax + By + Cz - D = 0^b$				
1	0.9720	0.1894	−0.1389	14.0338
2	0.9455	0.3198	−0.0612	14.5773
3	0.9660	0.2351	−0.1079	14.2607
4	−0.3097	0.9455	−0.1002	−0.0363

[a] This atom was not used in defining the plane. [b] Orthogonalized coordinates according to: Blow, D. M. *Acta Crystallogr.* 1960, *13*, 168.

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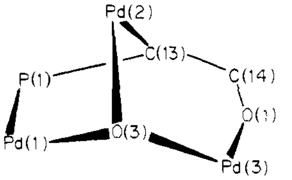
[22] Hartley, F. R. "The Chemistry of Platinum and Palladium"; Appl. Science Publishers Ltd.: London, 1973.

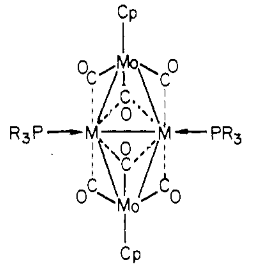
to formally assign the positive charge of the complex to either Pd(1) or Pd(3). The Pd(1)–, Pd(2)–, and Pd(3)–O(3) distances are 2.28 (1), 2.261 (8) and 2.144 (9) Å, respectively. The shorter Pd(3)–O(3) distance is best explained by the fact that it corresponds to a bond trans with respect to a nitrogen, whereas the other two Pd–O bonds are trans with respect to σ-bonded carbon atoms [C(26) and C(36)] of high trans influence. The dative O(1)–Pd(3) bond, which experiences the same situation, is comparatively shorter (2.17 (1) Å), indicating a stronger interaction. This parallels the previously noted activation of the ester function.

To our knowledge, such a bonding of an OH group to three palladium atoms appears unprecedented, but has been previously encountered in, e.g., Pt(IV) chemistry.[23]

Another way of looking at the molecular structure of **2** is illustrated below and considers the core of the molecule as derived from bicyclo[3.2.1]octane.



Complexes with [Mo(CO)$_3$Cp]$^-$ (Cp = η^5-C$_5$H$_5$). In a number of complexes, the Mo(CO)$_3$Cp group is bonded to a second metal M through a metal–metal bond only.[24] In some instances, the carbonyl ligands interact in a semibridging way with M while the contribution of the metal–metal interaction remains predominant.[25] We have recently found with the bimetallic complex Pd(8-mq)(PMe$_2$Ph) [Mo(CO)$_3$Cp] (**8**) that two carbonyl groups can be semibridging between the metals while these are at a relatively long distance of 3.059 (1) Å.[26] This illustrates the dilemna in deciding between direct or ligand-bridging metal–metal interactions. Furthermore, examples are now known where the Mo(CO)$_3$Cp moeity interacts with *two* other transition metal via metal–metal bonding (as shown by the relatively short metal–metal distances) and CO bridges. These are the planar triangulated clusters M$_2$Mo$_2$Cp$_2$(CO)$_6$(PR$_3$)$_2$ (M = Pd,[9,27] Pt[28,29])



M = Pd, Pt

and the trimetallic complex Pd$_2$(dmba)$_2$(μ-Cl)[μ-Mo(CO)$_3$Cp] (**7**).[3] In the former case, the Mo(CO)$_3$Cp group bridges a metal–metal bond (Pd–Pd = 2.582, Pt–Pt = 2.662 Å). In contrast, the Pd atoms in **7** are at a distance of 3.241 Å from each other, which does not correspond to a typical metal–metal interaction.

We have now prepared complex **3** in which the $\overset{\frown}{\mathrm{C\ N}}$ chelate is 8-mq (eq 2).

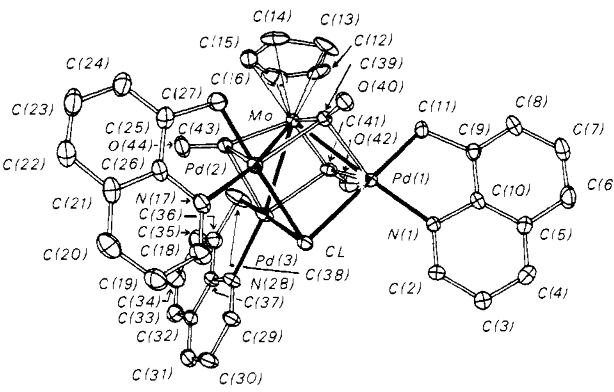
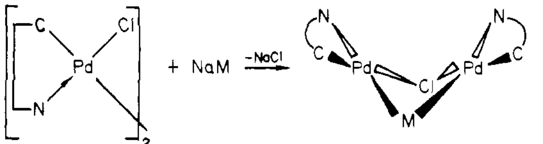


Figure 3. Structure of {[Pd(8-mq)]$_3$[μ_3-Mo(CO)$_3$Cp](μ_3-Cl)}BF$_4$ (**5a**).



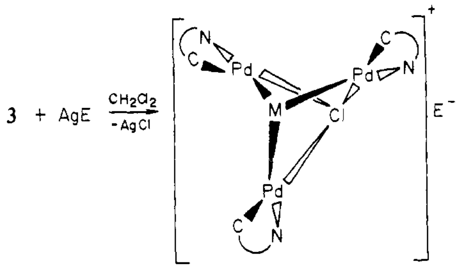
(2)

3, M = Mo(CO)$_3$Cp; $\overset{\frown}{\mathrm{C\ N}}$ = 8-mq

7, M = Mo(CO)$_3$Cp; $\overset{\frown}{\mathrm{C\ N}}$ = dmba

Unfortunately, **3** has a poor solubility in organic solvents and we could not obtain NMR spectra of sufficiently good quality. However, on the basis of its ν(CO) pattern and far-IR spectrum (see Experimental Section) it is most likely to have a geometry very similar to that of **7**.

Here, we present a new bonding type for the fragment Mo(CO)$_3$Cp, interacting in **5a** and **5b** with *three* other metals. As in **7**, the three other metals are not bonded to each other. Complexes **5a** and **5b** were synthesized by reacting **3** with silver salts in CH$_2$Cl$_2$ according to eq 3. The structure of **5a** has been determined by X-ray diffraction and is discussed below.



(3)

5a, E = BF$_4$; M = Mo(CO)$_3$Cp

5b, E = PF$_6$; M = Mo(CO)$_3$Cp

Description of the Molecular Structure of 5a. The molecular structure of the cation in **5** is shown in Figure 3. Crystal data, the positional coordinates, the interatomic distances and angles, and least-squares planes are given in Tables I, VIII, IX, and X, respectively. The BF$_4^-$ anion has a normal tetrahedral geometry and is not represented.

The cation can be viewed as an arrangement of three Pd atoms bridged by a Mo(CO)$_3$Cp moiety and a chloride ion. The coordination around each Pd atom is completed by a 8-mq chelate, of which the CH$_2$ groups are all trans with respect to Cl. The distortion away from square planar of the coordination of the Pd atoms (planes 1, 3, and 5, Table X) is evidenced by the distance of the carbon and nitrogen atoms of the 8-mq chelates to these planes (Table X). These distortions are probably due to solid-state interactions since the ^{1}H NMR spectrum of **5a** shows only a single resonance for the three CH$_2$ groups, as expected for a molecule containing three quivalent Pd(8-mq) metallocycles. In fact, the crystal structure indicates an approximate C_{3v} symmetry for the cation; thus the dihedral angles between the coordination planes of the Pd atoms are close to 120° (or its supplement, Table X). For comparison, the dihedral angle between the coordination

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[23] Hoff, G. R.; Brubaker, C. H. *Inorg. Chem.* **1968**, *7*, 1655; **1969**, *8*, 400.

[24] Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W. Ed.; Pergamon Press: Oxford, 1982; Chapter 40.

[25] See, for example: Braunstein, P.; Keller, E.; Vahrenkamp, H. *J. Organomet. Chem.* **1979**, *165*, 233.

[26] Pfeffer, M.; Grandjean, D.; Le Borgne, G. *Inorg. Chem.* **1981**, *20*, 4426.

[27] Bender, R.; Braunstein, P.; Dusausoy, Y.; Protas, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 596.

[28] Bender, R.; Braunstein, P.; Dusausoy, Y.; Protas, J. *J. Organomet. Chem.* **1979**, *172*, C51.

[29] Bender, R.; Braunstein, P.; Jud, J. M.; Dusausoy, Y., submitted for publication.

Table VIII. Positional Parameters and Their Estimated Standard Deviations for 5a

atom	*x*	*y*	*z*	*B*, Å$^{2\,a}$	atom	*x*	*y*	*z*	*B*, Å$^{2\,a}$
Pd(1)	0.39024 (2)	0.53817 (3)	0.30650 (3)	3.38 (1)	C(38)	0.3097 (4)	0.3765 (7)	0.4571 (5)	6.9 (3)
Pd(2)	0.30386 (2)	0.39238 (4)	0.20669 (3)	3.64 (1)	C(39)	0.4007 (3)	0.4279 (4)	0.2488 (4)	3.5 (2)
Pd(3)	0.29631 (2)	0.43522 (4)	0.36193 (3)	4.00 (1)	O(40)	0.4162 (2)	0.4420 (4)	0.1972 (3)	4.7 (1)
Mo	0.40086 (2)	0.38164 (4)	0.34404 (3)	3.00 (1)	C(41)	0.3956 (3)	0.4691 (5)	0.4111 (4)	3.7 (2)
Cl	0.27749 (7)	0.5208 (1)	0.2490 (1)	3.81 (4)	O(42)	0.4091 (3)	0.5056 (4)	0.4654 (3)	5.4 (2)
N(1)	0.3900 (2)	0.6580 (4)	0.2970 (4)	3.6 (1)	C(43)	0.3230 (3)	0.3234 (4)	0.3136 (5)	3.8 (2)
C(2)	0.3439 (3)	0.7066 (5)	0.2710 (5)	4.4 (2)	O(44)	0.2907 (3)	0.2692 (4)	0.3071 (4)	6.1 (2)
C(3)	0.3507 (4)	0.7857 (5)	0.2689 (6)	5.4 (2)	B	0.4508 (4)	1.0614 (6)	0.3666 (7)	5.3 (3)
C(4)	0.4069 (4)	0.8174 (5)	0.2951 (6)	5.2 (2)	F(1)	0.4565 (4)	0.9855 (4)	0.3555 (6)	11.3 (3)
C(5)	0.4572 (3)	0.7687 (5)	0.3228 (5)	4.4 (2)	F(2)	0.4852 (3)	1.0997 (4)	0.3378 (5)	11.6 (2)
C(6)	0.5185 (4)	0.7948 (6)	0.3490 (6)	6.2 (3)	F(3)	0.4714 (3)	1.0793 (5)	0.4404 (4)	9.9 (2)
C(7)	0.5636 (4)	0.7444 (6)	0.3701 (6)	5.9 (2)	F(4)	0.3933 (3)	1.0842 (5)	0.3357 (5)	9.9 (2)
C(8)	0.5530 (3)	0.6629 (5)	0.3694 (5)	4.6 (2)	HC2	0.3044	0.6856	0.2538	7*
C(9)	0.4949 (3)	0.6369 (4)	0.3456 (4)	3.3 (1)	HC3	0.3154	0.8180	0.2489	7*
C(10)	0.4479 (3)	0.6892 (5)	0.3209 (4)	3.6 (2)	HC4	0.4124	0.8713	0.2938	7*
C(11)	0.4804 (3)	0.5527 (5)	0.3472 (5)	4.2 (2)	HC6	0.5275	0.8481	0.3498	7*
C(12)	0.4905 (4)	0.3571 (6)	0.4399 (7)	7.5 (3)	HC7	0.6034	0.7630	0.3866	7*
C(13)	0.5007 (3)	0.3496 (6)	0.3758 (7)	9.3 (3)	HC8	0.5856	0.6281	0.3856	7*
C(14)	0.4653 (4)	0.2849 (6)	0.3389 (6)	7.8 (3)	H1C11	0.4968	0.5338	0.3968	7*
C(15)	0.4386 (4)	0.2608 (6)	0.3846 (8)	7.1 (3)	H2C11	0.4967	0.5247	0.3161	7*
C(16)	0.4533 (5)	0.3020 (7)	0.4431 (6)	7.8 (3)	HC12	0.5078	0.3965	0.4762	7*
N(17)	0.2191 (3)	0.3743 (4)	0.1190 (4)	4.3 (2)	HC13	0.5258	0.3791	0.3573	7*
C(18)	0.1709 (4)	0.4184 (6)	0.0962 (5)	5.3 (2)	HC14	0.4604	0.2636	0.2915	7*
C(19)	0.1149 (4)	0.3938 (6)	0.0472 (6)	6.3 (3)	HC15	0.4126	0.2172	0.3755	7*
C(20)	0.1091 (5)	0.3184 (7)	0.0195 (6)	6.8 (3)	HC16	0.4411	0.2972	0.4846	7*
C(21)	0.1596 (4)	0.2686 (6)	0.0436 (5)	5.6 (2)	HC18	0.1748	0.4695	0.1145	7*
C(22)	0.1589 (5)	0.1909 (6)	0.0233 (6)	6.8 (3)	HC19	0.0811	0.4281	0.0335	7*
C(23)	0.2094 (5)	0.1482 (6)	0.0494 (7)	7.0 (3)	HC20	0.0711	0.3022	−0.0150	7*
C(24)	0.2636 (5)	0.1791 (6)	0.0965 (6)	6.0 (3)	HC22	0.1229	0.1682	−0.0109	7*
C(25)	0.2676 (4)	0.2555 (5)	0.1170 (5)	4.8 (2)	HC23	0.2073	0.0951	0.0366	7*
C(26)	0.2152 (3)	0.2991 (5)	0.0918 (5)	4.4 (2)	HC24	0.2983	0.1476	0.1147	7*
C(27)	0.3243 (4)	0.2950 (6)	0.1628 (5)	5.2 (2)	H1C27	0.3462	0.3082	0.1325	7*
N(28)	0.2120 (3)	0.4571 (4)	0.3674 (4)	4.4 (2)	H2C27	0.3476	0.2623	0.2028	7*
C(29)	0.1661 (4)	0.4960 (6)	0.3208 (5)	5.0 (2)	HC29	0.1705	0.5185	0.2774	7*
C(30)	0.1131 (4)	0.5069 (6)	0.3336 (6)	5.5 (2)	HC30	0.0808	0.5361	0.2993	7*
C(31)	0.1074 (4)	0.4759 (6)	0.3952 (6)	5.8 (2)	HC31	0.0709	0.4835	0.4028	7*
C(32)	0.1533 (3)	0.4333 (5)	0.4459 (5)	4.6 (2)	HC33	0.1200	0.4090	0.5266	7*
C(33)	0.1525 (4)	0.4016 (6)	0.5120 (6)	6.4 (2)	HC34	0.1950	0.3354	0.5989	7*
C(34)	0.1986 (5)	0.3607 (7)	0.5561 (5)	7.1 (2)	HC35	0.2861	0.3249	0.5776	7*
C(35)	0.2518 (4)	0.3516 (6)	0.5424 (5)	5.9 (2)	H1C38	0.3173	0.3235	0.4497	7*
C(36)	0.2557 (4)	0.3828 (5)	0.4794 (5)	4.9 (2)	H2C38	0.3446	0.3970	0.4963	7*
C(37)	0.2070 (3)	0.4238 (5)	0.4312 (4)	4.0 (2)					

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab\cos\gamma\, B_{1,2} + ac\cos\beta\, B_{1,3} + bc\cos\alpha\, B_{2,3}]$.

planes of the Pd atoms in **7** is 55°. There is probably no bonding interaction to be found between the Pd atoms in **5a** in view of their large separations [Pd(1)–Pd(2), 3.369 (1) Å; Pd(1)–Pd(3), 3.332 (1) Å; Pd(2)–Pd(3), 3.132 (1) Å]. This is consistent with their description as Pd(II) centers (see later).

Selected structural data for the Pd(8-mq) metallocycles of **5a** and of the other compounds described in this work are presented in Table XI.

In view of the great similarities between the Pd(8-mq) metallocycles present in **2**, **5a**, and **6**, some of their structural characteristics (within the organic moiety) have been averaged.

These data are also compared with those reported for the other three complexes structurally characterized containing the Pd(8-mq) five-membered ring: complex **8**,[26] (8-mq)Pd[Ph$_2$PC(CO$_2$C$_2$H$_5$)C(O)OH],[2] and (8-mq)Pd(C$_{10}$H$_6$OCH$_3$).[30] The significant differences are found in the Pd–C and Pd–N bond distances, which depend very much on the nature of the ligand trans to these atoms.

The θ angle evaluates the puckering of the five-membered rings: it ranges from 1.5 to 19.5°.

The molybdenum atom is bonded to each palladium, the Pd–Mo distances (between 2.781 (1) and 2.800 (1) Å) being in the range of those found previously in **7**[3] and in the Pd$_2$Mo$_2$Cp$_2$(μ_3-CO)$_2$(μ_2-CO)$_4$ (PEt$_3$)$_2$ cluster[27] (abbreviated Pd$_2$Mo$_2$). The first example of a Mo(CO)$_3$Cp moiety bonded to three metal atoms is now established with **5a**. The geometry around the molybdenum is therefore also unique and deserves some comments.

As mentioned above, the three Pd atoms are roughly at the same distance from the Mo center. The MoPd$_3$ framework forms a distorted tetrahedron and each carbonyl group caps an open Pd$_2$Mo triangular face in a "semi triply bridged" mode. In both **7** and Pd$_2$Mo$_2$, only one CO per molybdenum was found in such a bridging position. The Mo–C–O angles (mean 158°) and the Mo–C bond lengths (mean 2.015 Å) are very close to those found in **7** and in Pd$_2$Mo$_2$ for the μ_3-CO. However, the palladium–carbon (CO) separations (average 2.28 Å) are significantly shorter than the corresponding ones in **7** (average 2.38 Å) or in Pd$_2$Mo$_2$ (average 2.31 Å).

Selected structural parameters concerning the interactions of the carbonyl ligands with the three MoPd$_2$ faces of **5a** are given in Figure 4.

The C–Mo–C angles (av 106.3°) indicate a very important flattening of the Mo(CO)$_3$ tripod when compared to all reported structures containing the Mo(CO)$_3$Cp fragment such as CpMo(CO)$_3$X,[31] CpMo(CO)$_3^-$;[32] **7**,[3] or Pd$_2$Mo$_2$.[27] The η^5-cyclopentadienyl ligand is at a typical distance from the Mo atom (1.995

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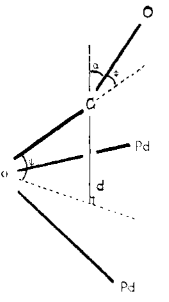
[30] Dehand, J.; Mauro, A.; Ossor, H.; Pfeffer, M.; De A. Santos, R. H.; Lechat, J. R. *J. Organomet. Chem.* **1983**, *250*, 537.

[31] See, for example: Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197 and references therein.

[32] (a) Crotty, D. E.; Corey, E. R.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *Inorg. Chem.* **1977**, *16*, 920. (b) Janta, R.; Albert, W.; Rössner, H.; Malisch, W.; Langenbach, H. J.; Röttinger, E.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 2729.

Table IX. Selected Interatomic Distances (Å) and Angles (deg) in {[Pd(8-mq)]$_3$[μ_3-Mo(CO)$_3$(η^5-C$_5$H$_5$)](μ_3-Cl)}BF$_4$ (5a)

Mo-Pd(1)	2.791 (1)	Pd(1)-Mo-Pd(2)	74.24 (2)
Mo-Pd(2)	2.791 (1)	Pd(1)-Mo-Pd(3)	73.14 (2)
Mo-Pd(3)	2.800 (1)	Pd(2)-Mo-Pd(3)	68.14 (2)
Pd(1)-Cl	2.520 (2)	Pd(1)-Cl-Pd(3)	83.80 (5)
Pd(2)-Cl	2.525 (2)	Pd(1)-Cl-Pd(3)	82.78 (5)
Pd(3)-Cl	2.520 (2)	Pd(2)-Cl-Pd(3)	76.77 (5)
C(39)-Mo	1.991 (8)	Pd(1)-C(39)-O(40)	110.6 (5)
C(39)-Pd(1)	2.266 (7)	Pd(2)-C(39)-O(40)	110.7 (5)
C(39)-Pd(2)	2.235 (7)	Mo-C(39)-O(40)	159.8 (6)
C(39)-O(40)	1.200 (9)		
C(41)-Mo	2.020 (8)	Pd(1)-C(41)-O(42)	114.0 (6)
C(41)-Pd(1)	2.295 (8)	Pd(3)-C(41)-O(42)	114.4 (6)
C(41)-Pd(3)	2.279 (7)	Mo-C(41)-O(42)	156.9 (6)
C(41)-O(42)	1.156 (9)		
C(43)-Mo	2.020 (8)	Pd(2)-C(43)-O(44)	114.5 (6)
C(43)-Pd(2)	2.264 (7)	Pd(3)-C(43)-O(44)	115.6 (6)
C(43)-Pd(3)	2.279 (7)	Mo-C(43)-O(44)	157.3 (6)
C(43)-O(44)	1.193 (8)	N(1)-Pd(1)-Cl	92.5 (1)
		N(1)-Pd(1)-Mo	170.7 (2)
Pd(1)-N(1)	2.083 (6)	N(1)-Pd(1)-C(11)	83.0 (2)
Pd(1)-C(11)	2.014 (7)	Cl-Pd(1)-Mo	88.67 (4)
Pd(2)-N(17)	2.118 (6)	Cl-Pd(1)-C(11)	177.1 (2)
Pd(2)-C(27)	2.023 (9)	Mo-Pd(1)-C(11)	92.2 (2)
Pd(3)-N(28)	2.089 (6)		
Pd(3)-C(39)	2.006 (9)	N(17)-Pd(2)-Cl	96.1 (2)
		N(17)-Pd(2)-Mo	162.0 (2)
Pd(1)···Pd(2)	3.369 (1)	N(17)-Pd(2)-C(27)	81.6 (3)
Pd(1)···Pd(3)	3.332 (1)	Cl-Pd(2)-Mo	88.57 (4)
Pd(2)···Pd(3)	3.132 (1)	Cl-Pd(2)-C(27)	174.1 (3)
		Mo-Pd(2)-C(27)	95.3 (2)
B-F(1)	1.34 (1)		
B-F(2)	1.32 (1)	N(28)-Pd(3)-Cl	93.9 (2)
B-F(3)	1.35 (1)	N(28)-Pd(3)-Mo	170.2 (2)
B-F(4)	1.34 (1)	N(28)-Pd(3)-C(38)	83.0 (3)
		Cl-Pd(3)-Mo	88.45 (4)
C(39)-Mo-C(41)	107.5 (3)	Cl-Pd(3)-C(38)	174.2 (4)
C(39)-Mo-C(43)	104.5 (3)	Mo-Pd(3)-C(38)	95.4 (2)
C(41)-Mo-C(43)	107.0 (3)		
Pd(1)-C(39)-Pd(2)	96.9 (2)	C(39)-Pd(1)-C(41)	90.3 (3)
Pd(1)-C(41)-Pd(3)	93.5 (2)	C(39)-Pd(1)-Cl	88.8 (2)
Pd(2)-C(43)-Pd(3)	85.8 (2)	C(41)-Pd(1)-Cl	91.3 (2)
Pd(1)-C(39)-Mo	81.6 (2)	C(39)-Pd(2)-C(43)	89.1 (2)
Pd(2)-C(39)-Mo	82.4 (2)	C(39)-Pd(2)-Cl	89.4 (2)
Pd(1)-C(41)-Mo	80.3 (3)	C(43)-Pd(2)-Cl	99.5 (2)
Pd(3)-C(41)-Mo	81.1 (2)	C(41)-Pd(3)-C(43)	88.9 (2)
Pd(2)-C(43)-Mo	81.5 (2)	C(41)-Pd(3)-Cl	91.7 (2)
Pd(3)-C(43)-Mo	80.1 (2)	C(43)-Pd(3)-Cl	97.8 (2)



Parameters \ Metallic faces	5a: MoPd(1)Pd(2)	5a: MoPd(1)Pd(3)	5a: MoPd(2)Pd(3)	**2** Ref.(3)	Pd$_2$Mo$_2$ Ref.(27)
ψ (°)	41.0	42.7	44.6	47	49
φ (°)	20.2	23.1	22.7	24	23.5
α (°)	29.5	24.2	22.7	19	17.2
d (Å)	1.306(8)	1.369(8)	1.419(8)	1.500(12)	1.54(1)

Figure 4. Selected structural parameters for the interactions of the CO ligands with the trimetallic faces of **5a** and related compounds.

Å). It is parallel to the plane of the three carbonyl carbon atoms and of the three Pd atoms. Therefore, the Mo(CO)$_3$Cp fragment

Table X. Least-Squares Planes for {[Pd(8-mq)]$_3$[μ_3-Mo(CO)$_3$(η^5-C$_5$H$_5$)](μ_3-Cl)}BF$_4$ (5a)

plane no.	atoms	distance from plane, Å	plane no.	atoms	distance from plane, Å
1	Pd(1)	0.003 (1)	6	Pd(3)	0.000 (1)
	N(1)	−0.272 (6)		N(28)	0.000 (7)
	C(11)	0.101 (9)		C(38)	0.000 (12)
	Mo	−0.002 (1)		C(36)[a]	−0.043 (9)
	Cl	0.002 (1)		C(37)[a]	−0.027 (8)
2	Pd(1)	0.000 (1)	7	C(12)	0.005 (11)
	N(1)	0.000 (6)		C(13)	−0.004 (11)
	C(11)	0.000 (9)		C(14)	0.001 (11)
	C(9)[a]	0.033 (7)		C(15)	0.002 (11)
	C(10)[a]	0.010 (7)		C(16)	−0.004 (12)
3	Pd(2)	0.007 (1)	8	C(39)	0.000 (8)
	N(17)	−0.615 (7)		C(41)	0.000 (8)
	C(27)	0.170 (10)		C(43)	0.000 (8)
	Mo	−0.004 (1)		O(40)[a]	0.051 (6)
	Cl	0.002 (12)		O(42)[a]	−0.017 (7)
				O(44)[a]	−0.005 (7)
4	Pd(2)	0.000 (1)			
	N(17)	0.000 (7)	9	Pd(1)	0.000 (1)
	C(27)	0.000 (10)		Pd(2)	0.000 (1)
	C(25)[a]	−0.454 (9)		Pd(3)	0.000 (1)
	C(26)[a]	−0.365 (8)			
5	Pd(3)	−0.004 (1)			
	N(28)	0.335 (7)			
	C(38)	−0.156 (11)			
	Mo	0.002 (1)			
	Cl	−0.003 (2)			

Dihedral Angles between the Planes

plane	angle, deg	plane	angle, deg
1-2	8.5	3-5	111
1-3	54.1	5-6	10.9
1-5	56.9	7-8	2.1
3-4	18.6	7-9	3.5
		8-9	5.4

Equations of the Planes of the Form $Ax + By + Cz - D = 0$[b]

plane	A	B	C	D
1	0.4227	−0.2167	−0.8800	−3.7984
2	0.3704	−0.0858	−0.9249	−3.1938
3	0.7893	0.4640	−0.4022	6.2339
4	0.5627	0.5517	−0.6157	4.7421
5	−0.3287	−0.7309	−0.5980	−10.8313
6	−0.1780	−0.8265	−0.5340	−10.4650
7	−0.6510	0.6035	−0.4603	−5.4611
8	−0.6782	0.5849	−0.4449	−2.9230
9	−0.6090	0.6479	−0.4575	−0.8025

[a] This atom was not used in defining the plane. [b] Orthogonalized coordinates according to: Blow, D. M. *Acta Crystallogr.* 1960, *13*, 168.

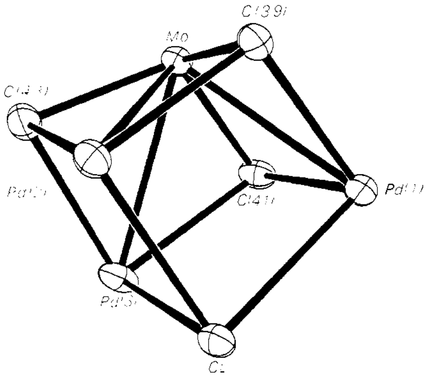


Figure 5. Cubane-like structure of the inorganic core of **5a**.

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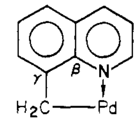
(33) See, for example: Miller, J. R. *Adv. Inorg. Chem. Radiochem.* **1962**, *4*, 133.

Table XI. Selected Structural Data for the Cyclopalladated 8-Methylquinoline Chelate



	2			5a[a]	6	8	(8-mq)Pd-($C_{10}H_6OCH_3$)[f]	(8-mq)Pd[Ph_2PC-($CO_2C_2H_5$)C(O)OH][g]
atom trans to CH_2	O[b]	O[b]	O[c]	Cl	Br	Mo	O	O
atom trans to N	P	C	O[b]	Mo	P	P	C	P
Pd-CH_2, Å	2.03 (1)	2.06 (2)	2.01 (1)	2.014 (9)	2.046 (6)	2.074 (12)	1.986 (5)	2.05 (2)
Pd-N, Å	2.15 (1)	2.06 (2)	1.99 (1)	2.097 (6)	2.094 (5)	2.150 (7)	2.127 (6)	2.07 (2)
CH_2-Pd-N, deg	81.2 (6)	86.2 (6)	83.7 (6)	82 (5)	81.9 (2)	82.0 (4)	82.8 (2)	83.5 (9)
θ,[d] deg	16.7	19.5	4.9	1.5 18.0 1.9	7.7	-	7.9	-
N-$^{\alpha}$C, Å			1.30 (2)[e]			1.306 (15)	1.317 (7)	1.35 (3)
N-$^{\beta}$C, Å			1.37 (2)[e]			1.414 (13)	1.380 (9)	1.38 (3)
$^{\gamma}$C-CH_2, Å			1.51 (4)[e]			1.514 (14)	1.491 (8)	1.49 (3)
C$\overset{...}{-}$C, Å			1.38 (4)[e]			1.396 (16)	1.389 (9)	1.41 (3)
Pd-N-$^{\beta}$C, deg			112 (2)[e]			111.0 (6)	111.5 (3)	113 (1)
N-$^{\beta}$C-$^{\gamma}$C, deg			116 (2)[e]			-	116.2 (5)	115 (2)
$^{\beta}$C-$^{\gamma}$C-CH_2, deg			117 (3)[e]			-	-	118 (1)
$^{\gamma}$C-CH_2-Pd, deg			108 (4)[e]			-	109.7 (4)	108 (2)
ref			this work			(8)	(30)	(2)

[a] Except for θ, the data represent the mean values between the three chemically equivalent Pd(8-mq) rings. [b] O of the μ_3-OH group. [c] O of the C=O group of the phosphine ligand. [d] Dihedral angle between the plane of the quinoline and the plane defined by Pd, N, and C of the CH_2 group. [e] Mean values for compounds **2**, 5a, and 6 with rms = $[1/n - 1)] \Sigma_{i=1}^{n} |d_i - \bar{d}|$. [f] $C_{10}H_6OCH_3$ = 1-methoxynaphthalene-8-C,O. [g] The data represent the mean values between two molecules of the unit cell.

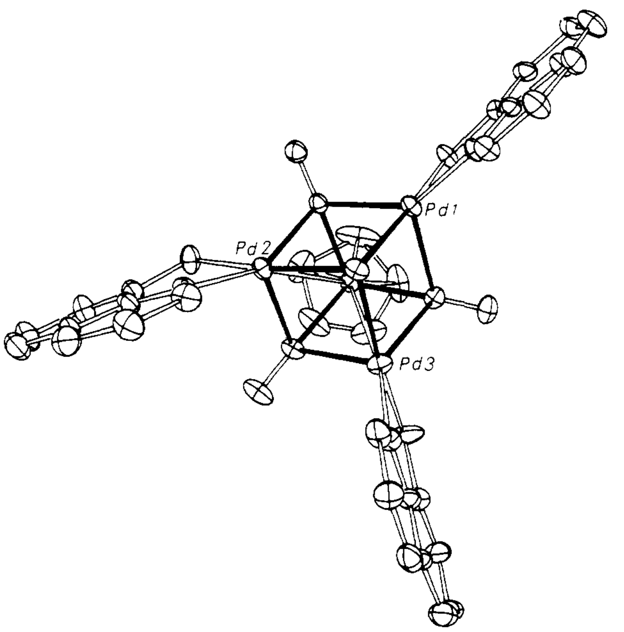


Figure 6. Structure of **5a** viewed along the Mo-centroid Cp axis.

retains some of its classical structural features for a three-legged piano stool, despite the presence of three Pd atoms within the $Mo(CO)_3$ cone angle.

Although examples of triply bridging halides between transition metals are known in the literature,[33] to our knowledge no structural data seem to have been reported for them in the case of Pd complexes. Here, all the Pd–Cl bond lengths are identical (2.522 Å, Table IX) and, as expected, somewhat longer than in **7** (average 2.462 Å)[29] where the chloride bridges only two Pd atoms; this is also consistent with the fact that in **5a** Cl is trans with respect to three CH_2 groups of strong trans influence.

On the basis of its pseudo C_{3v} symmetry, the inorganic core of the cation in **5a** could be viewed as a $MoPd_3$ distorted tetrahedron in which the four faces are capped by the three carbonyls and the chloride. A more complete and perhaps better description is that of a distorted cubane-like structure involving the four metal atoms, Cl, C(39), C(41), and C(43) (Figures 5 and 6). This is supported by the values of the angles at the corners of the cube (Table IX).

The slight deviation from pseudo-C_{3v} symmetry of the $\overset{\frown}{C\,N}$ chelate on Pd(2) (Figure 6) might be related to packing forces in the crystal (Figure 7).

The structure of **5a** having been unambiguously established, it is now possible to discuss the chemistry of its synthesis (eq 3). Thus, **5a** appears to derive from the condensation of a Pd(8-mq)$^+$

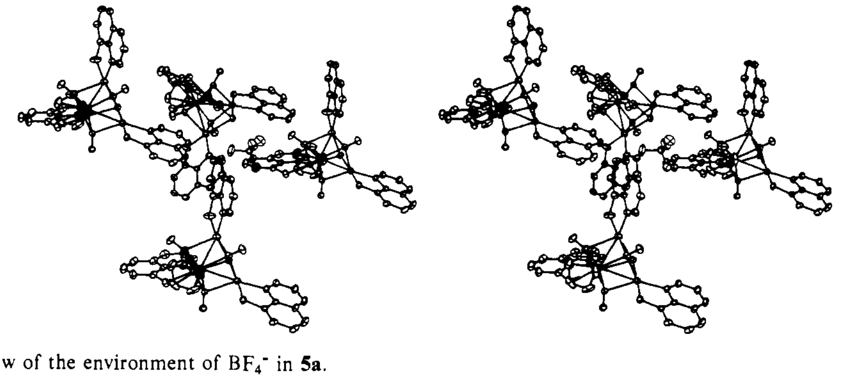


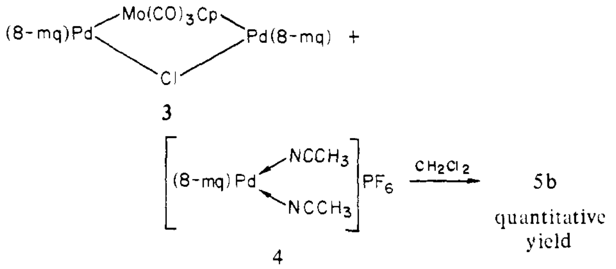
Figure 7. Stereoscopic view of the environment of BF_4^- in **5a**.

Table XII. Selected Structural Data for the Coordinated Functional Ligands $Ph_2P\text{-}^{\alpha}CH_2\text{-}^{\beta}C(O)OC_2H_5$ (L) and $[Ph_2P\text{-}^{\alpha}CH\text{-}^{\beta}C(O)OC_2H_5]^-$ (L^-)

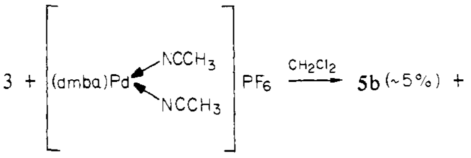
complex	coordination mode of the ligand	distances, Å metal-P	P-$^{\alpha}$C	$^{\alpha}$C-$^{\beta}$C	$^{\beta}$C-O(C_2H_5)	$^{\beta}$C=O	metal-O(=C)	metal-$^{\alpha}$C	ref
$Pd(8\text{-mq})Br(Ph_2PCH_2COOC_2H_5)$ (**6**)	[η^1-P] L	2.232 (1)	1.836 (6)	1.530 (9)	1.328 (8)	1.173 (9)	-	-	this work
trans-$RuCl_2[Ph_2PCH_2C(O)OC_2H_5][Ph_2PCH_2C(O)OC_2H_5]_2$	[η^1-P] L	2.403 (1)^a	1.862 (4)	1.517 (6)	1.320 (6)	1.188 (6)	-	-	35
		2.266 (1)^b	1.868 (4)	1.528 (6)	1.331 (6)	1.170 (6)	-	-	
	[η^2-P,O] L	2.363 (1)	1.863 (4)	1.504 (5)	1.320 (5)	1.222 (4)	2.230 (3)	-	
$Pd(dmba)[Ph_2PCHC(O)OC_2H_5]$	[η^2-P,O] L^-	2.242 (2)	1.751 (9)	1.37 (1)	1.36 (1)	1.27 (1)	2.117 (5)	-	2
$[Pd(dmba)]_2(\mu\text{-}Cl)(\mu\text{-}Ph_2PCHC(O)OC_2H_5)$	μ_2-[P,C] L^-	2.233 (6)	1.81 (2)	1.52 (3)	1.39 (2)	1.15 (2)	-	2.01 (2)	2
$\{[Pd(8\text{-mq})]_3(\mu_3\text{-}OH)(\mu_3\text{-}Ph_2PCHCOOC_2H_5)\}PF_6$ (**2**)	μ_3-[P,C,O] L^-	2.231 (4)	1.81 (1)	1.48 (2)	1.31 (2)	1.23 (2)	2.17 (1)	2.06 (1)	this work

[a] This ligand is trans with respect to the phosphorus of the chelating L. [b] This ligand is trans with respect to the oxygen of the chelating L.

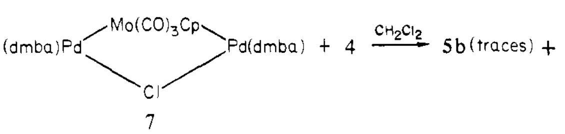
moiety with **3**. The former unit would result from the decomposition of the unstable species produced by halide abstraction on **3**. This is confirmed by the following experiment. The solvento-complex $[Pd(8\text{-mq})(CH_3CN)_2]PF_6$ (**4**) was separately prepared and reacted with 1 equiv of **3** in CH_2Cl_2. A very clean reaction proceeded, affording **5b** in almost quantiative yields (eq 4). This also illustrates the donor character of **3** toward appropriate electrophiles, such as the 12-electron $Pd(8\text{-mq})^+$ cation. This occurs by increasing the formal electron contribution of the Cl and $Mo(CO)_3Cp$ bridges from three each in **3** to five each in **5** (see below). Since the possibility of the stepwise formation of **5** had been demonstrated by reaction 4, we envisaged producing a series of new complexes similar to **5b** but containing two *different* types of C⌒N chelates in the tetrametallic cation. Ideally, such complexes were concieved to result from the reactions of **3** or **7** with the mononuclear Pd(II) solvento-complexes $[Pd(dmba)(CH_3CN)_2]^+$ or $[Pd(8\text{-mq})(CH_3CN)_2]^+$, respectively. This approach could allow a better evaluation of the influence of the organometallic chelate C⌒N on the reactivity and stability of the molecules involved. Unfortunately, all our attempts to prepare such mixed C⌒N complexes failed, and the incorporation of a Pd(dmba) unit into the tetrametallic complexes was found to be impossible under our conditions. For instance, reaction of $[Pd(dmba)(CH_3CN)_2]^+$ with **3** gave some **5b**[34] and decomposition products (eq 5). Similarly, the cross experiment (eq 6) was mainly unsuccessful. This exemplifies the determining role of the C⌒N chelates in these systems.



(4)



decomposition products (5)



decomposition products (6)

In summary, we emphasize the similarities between reactions 1 and 2. (i) They are both nonstoichiometric and only **2** and **5** could be isolated. (ii) Abstraction of the bridging chloride in **1** and **3** follows a similar route in which the molecules are destabilized and produce the unsaturated $Pd(8\text{-mq})^+$ unit, which further adds on some unreacted **1** and **3** to form **2** and **5**, respectively. (iii) When these reactions were carried out with compounds having an ancillary ligand different from 8-mq (on $Pd(dmba)(\mu\text{-}Cl)[\mu\text{-}Ph_2PCH(COOC_2H_5)]Pd(dmba)$ or on **7**), no complex analogous to **2** and **5**, respectively, could be isolated and only decomposition products were observed. This illustrates the greater stability that the 8-mq ligand confers to the final products. Furthermore, despite their obvious differences, similarities between

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[34] Formation of **5b** is accounted here by the reaction of **3** with **4**, itself generated by decomposition of the hypothetical $\{[Pd_3(8\text{-mq})_2(dmba)](\mu_3\text{-}Cl)(\mu_3\text{-}Mo(CO)_3Cp)\}^+$, similar to **5b**. This is supported by the related observation that $[Pd(dmba)(CH_3CN)_2]^+$ reacts with $[Pd(8\text{-mq})(\mu\text{-}Cl)]_2$ in CH_2Cl_2 to afford **4** and $[Pd(dmba)(\mu\text{-}Cl)]_2$.

[35] Braunstein, P.; Matt, D.; Dusausoy, Y. *Inorg. Chem.* **1983**, *22*, 2043.

2 and 5 deserve some comments. In both complexes, the palladium atoms are not directly bonded to each others through Pd–Pd bonds but linked by bridging ligands. Whereas the five-electron donor ligands μ_3-OH in 2 and μ_3-Cl in 5 are of a conventional type, the μ_3-[$Ph_2PCHC(O)OC_2H_5$] and μ_3-[$Mo(CO)_3Cp$] bridges also have to be described as five-electron donors in order to account for the structures of 2 and 5 involving three square-planar Pd(II) centers. Although this bonding mode could be predicted in the former case, and is easily rationalized with localized two-electron–two-center bonds, it was not so in the latter case. Indeed, **5a** is the only example known of such a bonding situation for the organometallic fragment $Mo(CO)_3Cp$. The question remains open as to what extent the electrons from the three carbonyls and the d electrons from the molybdenum are involved in the bonding of the $Mo(CO)_3Cp$ fragment to the three Pd(II) centers.

Acknowledgment. We thank the Centre National de la Recherche Scientifique for financial support.

Registry No. 1, 79086-58-1; **2**, 87862-44-0; **3**, 87862-45-1; **4**, 87862-47-3; **5a**, 87862-49-5; **5b**, 87935-86-2; **6**, 79061-46-4; Na[$Mo(CO)_3$-(η^5-C_5H_5)], 12079-69-5; [Pd(8-mq)Cl]$_2$, 28377-73-3; $AgBF_4$, 14104-20-2; $AgPF_6$, 26042-63-7.

Supplementary Material Available: Least-squares planes of the quinoline rings for compounds **2** and **5a** (Tables SI and SII), anisotropic thermal parameters for **2**, **5a**, and **6** (Tables SIII, SIV, and SV), and observed and calculated structure factors for **2**, **5a**, and **6** (Tables SVI, SVII, and SVIII) (60 pages). Ordering information is given on any current masthead page.

Communications to the Editor

α vs. β Protonation of Pyrrole and Indole

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α vs. β protonation of five-membered rings has been the subject of considerable attention,[1-6] in particular regarding pyrrole and its derivatives. It is well established, at least in solution, that electrophilic substitution of these compounds takes place predominantely at the α position,[1,5] although all theoretical calculations,[7] both at the semiempirical and the "ab initio" levels, assign a larger electronic charge to the β than to the α position. Moreover, the corresponding molecular electrostatic potentials[2] indicate a favorable β attachment, and as a consequence, some complicated mechanisms involving a simultaneous bending of the $C_\alpha H$ and the NH bonds out of the molecular plane or the behavior of the nitrogen atom as a charge transducer have been proposed[2] to explain the predominance of the α substitution in pyrrole.

It is worth noting however that when this five-membered ring is fused to a six-membered one, as in indole, both the experimental evidences[8] and the theoretical calculations[9] indicate that C_3 (β position) is the most reactive center toward electrophilic reagents.

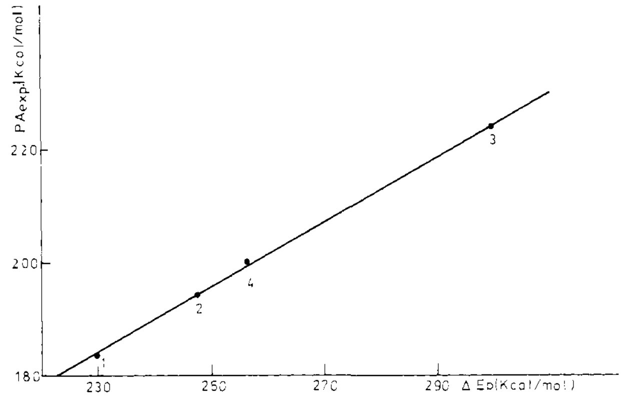

Figure 1. Experimental PA vs. calculated protonation energies.

We aim at showing, in this paper, that this question can be clarified from a theoretical point of view.

First, it must be indicated that the different theoretical approaches reported in the literature to evaluate proton affinities or to predict preferred protonation sites can be classified in two different categories: those that would furnish information on the most active center for kinetically controlled processes and those that would indicate which protonated species is thermodynamically the most stable.

It is well-known that (a) the molecular electrostatic potentials or (b) the linear correlation between gas-phase proton affinities (PA) and 1s binding energies[10] (or 1s "ab initio" orbital energies[3]) provides, in general, good tools to predict the preferred protonation site of a given compound. However, it must be taken into account that, for instance, the molecular electrostatic potential furnished information on the most favorable approaching path to the isolated molecule of a unit positive charge, but the corresponding substitution does not lead necessarily to the most stable isomer. Similarly, procedure b yields the *intrinsic basicity* of a given center of the isolated molecule, but quite frequently protonation induces dramatic changes in both the structure and the charge distribution of the system. As a consequence, not always does protonation on the most basic center lead to the most stable protonated form.

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