Notes

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Reactivity of Cyclopalladated Compounds. 6.[1] Synthesis of Heterodimetallic Species with Pd–Co, Pd–Mo, or Pd–Fe Bonds. X-ray Crystal Structure of (Dimethylphenylphosphine)tricarbonyl(η-cyclopentadienyl)molybdenum(8-methylquinoline-*C*,*N*)palladium(II)(*Pd–Mo*)

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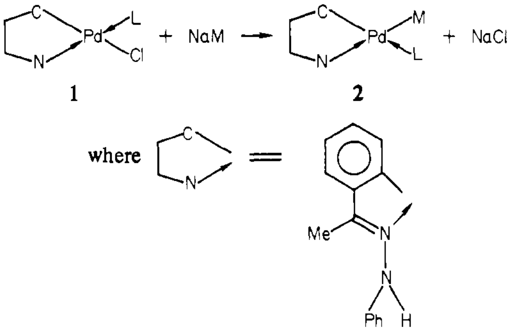
We have previously shown[3] that heterodimetallic species containing a metal–metal bond can be synthesized by reacting carbonylmetalate anions with monomeric cyclopalladated compounds according to reaction 1.



1 2

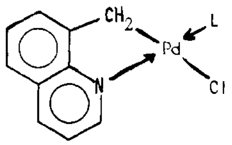
$M = Co(CO)_4$ (**2a**), $Mo(CO)_3(\eta\text{-}C_5H_5)$ (**2b**)
L = pyridine

The crystal structure of compound **2a** showed that the $Co(CO)_4$ moiety lies in a position trans to the nitrogen atom of the cyclopalladated ligand.[3b] We ascribed the concomitant migration of the pyridine in the position trans to the σ-bonded carbon to steric factors, that latter position being much more sterically hindered than the former one. In addition, we could not synthesize dimetalic species of type **2** when L is a phosphine ligand. In order to get definitive information about the steric effects around the C–N ligand in that reaction, we have carried out the present study. We have now chosen 8-methylquinoline as the cyclopalladated ligand since it has similar steric effects at the position trans to the σ-bonded carbon and to the nitrogen atom.

Experimental Section

The reaction conditions are the same than those described in a previous paper.[3a] Infrared spectra were recorded on a Perkin-Elmer 398 spectrophotometer. ^1H NMR spectra were recorded on a FT-Bruker WH-90 or a Cameca 250 instrument at 90 or 250 MHz, respectively; the chemical shifts are downfield relative to external Me_4Si. The elemental analysis of C, H, and N were performed by the Service Central de Microanalyses du CNRS.

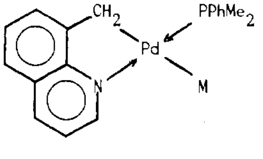
Syntheses. The starting materials **3a**–**3c** were prepared by published methods.[4,5] All new compounds give satisfactory analyses. The spectroscopic data (IR and ^1H NMR) are given in Table I.



3a L = Py
3b L = 4-MePy
3c L = $PPhMe_2$
3d L = CO

$Pd(NC_9H_6CH_2)COCl$ (3d). Carbon monoxide is bubbled through a well-stirred suspension of μ-dichloro-bis(8-methylquinoline-*C*,*N*)-dipalladium in THF for 10 min during which time the yellow suspension gradually turns white. It is then filtered, washed with ether, and dried; the yield is quantitative. **3d** thus obtained is stable in air for a long period of time (several months) whereas solution of **3d** is only stable in the presence of CO for 1 or 2 h.

$Pd(8\text{-}mq)PPhMe_2M$ ($M = Mo(CO)_3(\eta\text{-}C_5H_5)$, $Co(CO)_4$) (4a, 4b).

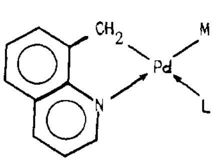


4a M = $Mo(CO)_3(\eta\text{-}C_5H_5)$
4b M = $Co(CO)_4$

To a stirred solution of 842 mg (2 mmol) of **3c** in THF is added 50 mL of a 0.04 M solution of NaM in THF. No change of the color of the solution is visible after 2 h. Moreover, an infrared spectra of the solution shows that the carbonylmetalate anion is unreacted.

The THF is then removed under reduced pressure until a yellow oil is obtained. This oil is washed with hexane, affording an orange precipitate which is dried in vacuo and washed again with water and vacuum dried. The compounds **4** are obtained from that powder as red prisms (**4a**) or orange crystals (**4b**) from a CH_2Cl_2–pentane solution at −20 °C (yield 40%).

$Pd(8\text{-}mq)(4\text{-}MePy)Mo(CO)_3(\eta\text{-}C_5H_5)$ (5a) and $Pd(8\text{-}mq)PyM$ ($M = Co(CO)_4$, $Fe(CO)_3NO$) (5b, 5c). A 50-mL sample of a 0.04 M solution of NaM ($M = Mo(CO)_3(\eta\text{-}C_5H_5)$, $Co(CO)_4$) or $KFe(CO)_3NO$ is added to a stirred suspension of 2 mmol of **3b** or **3a** in 20 mL of THF at room temperature. The color of the solution turns instantaneously red, and the suspension of **3b** or **3a** disappears in ca. 10 min. The solution is filtered to eliminate the NaCl, and the THF



5a L = 4-MePy, M = $Mo(CO)_3(\eta\text{-}C_5H_5)$
5b L = Py, M = $Co(CO)_4$
5c L = Py, M = $Fe(CO)_3NO$
5d L = CO, M = $Mo(CO)_3(\eta\text{-}C_5H_5)$
5e L = CO, M = $Co(CO)_4$

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[1] Part V: Bahsoun, A.; Dehand, M.; Pfeffer, M.; Zinsius, M.; Bouaoud, S. E.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* **1979**, 547.

[2] (a) Université Louis Pasteur. (b) Université de Rennes.

[3] (a) Dehand, J.; Pfeffer, M. *J. Organomet. Chem.* **1976**, *104*, 377. (b) Le Borgne, G.; Bouaoud, S. E.; Grandjean, D.; Braunstein, P.; Dehand, J.; Pfeffer, M. *Ibid.* **1977**, *136*, 375.

[4] Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1978**, 344.

[5] See, for example: Dehand, J.; Pfeffer, M.; Zinsius, M. *Inorg. Chim. Acta* **1975**, *13*, 299.

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Table I. Spectroscopic Data

compds	IR data (ν(CO), cm^{-1})		^{1}H NMR^a shifts					
	KBr	THF	H$^{2\,b}$	H^4	H arom	C_5H_5	CH_2	others
Pd(8-mq)COCl^c (**3d**)	2108 s		9.54 (dd, $^3J_{H^2H^3} = 4.9$)	8.47 (dd, $^3J_{H^3H^4} = 8.3$)	7.82-7.60		3.95	
Pd(8-mq)(PPhMe$_2$)Mo(CO)$_3$Cp (**4a**)	1882 vs, 1782 vs, 1775 vs	1900 vs, 1812 vs, 1790 vs	9.18 (m)	8.34 (m)	7.94-7.60	4.81 (s)	3.50 (m)	1.85 (d, CH_3, $^2J_{PH} = 10.3$)
Pd(8-mq)(PPhMe$_2$)Co(CO)$_4$ (**4b**)	2005 vs, 1932 vs, 1898 vs, 1872 vs	2022 vs, 1940 vs, 1921 vs, 1887 vs	9.33 (m)	8.33 (dd, $^3J(H^3H^4) = 8.3$)	7.78-7.48		3.41 (d, $^3J_{PH} = 3.8$)	1.92 (d, CH_3, $^2J_{PH} = 10.6$)
Pd(8-mq)(4-Mepy)Mo(CO)$_3$Cp (**5a**)	1887 vs, 1780 vs br	1900 vs, 1975 vs br	8.69 (m)	8.23 (dd, $^3J_{H^3H^4} = 8.8$)	7.67-7.16	5.26 (s)	2.89 (s)	2.39 (s, CH_3)
Pd(8-mq)pyCo(CO)$_4$ (**5b**)	2017 vs, 1943 vs, 1872 s br	2020 s, 1947 vs, 1878 s	8.80 (m)	8.35 (dd, $^3J_{H^3H^4} = 9.5$)	7.87-7.23		3.10 (s)	
Pd(8-mq)pyFe(CO)$_3$NO^d (**5c**)	1980 vs, 1962 vs, 1860 vs br	1982 vs, 1905 s, 1865 vs	8.51 (m)	7.44 (dd, $^3J_{H^3H^4} = 8.2$)	7.3-6.2		3.42 (s)	
Pd(8-mq)(CO)Mo(CO)$_3$Cp (**5d**)	2065 vs, 1915 vs, 1830 vs, 1812 vs	2062 s, 1925 vs, 1827 vs	9.07 (dd, $^3J_{H^2H^3} = 5.0$)	8.35 (dd, $^3J_{H^3H^4} = 12.2$)	7.71-7.49	5.34 (s)	3.89 (s)	
Pd(8-mq)(CO)Co(CO)$_4$ (**5e**)	2090 vs, 2030 vs, 1972 s, 1934 s, 1913 vs	2098 m, 2030 vs, 1960 s, 1940 s, 1918 vs	9.34 (dd, $^3J_{H^2H^3} = 5.3$)	8.50 (dd, $^3J_{H^3H^4} = 8.3$)	7.84-7.64		4.19 (s)	

[a] In CD_2Cl_2 solutions except **5a** and **5d** in $CDCl_3$ and **5c** in C_6D_6. *J* in Hz. [b] H^2 and H^4 are the ortho and the para protons, respectively, of the 8-methylquinoline (8-mq) cyclopalladated ligand. For all the compounds, $1.5 \leqslant {}^4J_{H^2H^4} \leqslant 1.9$ Hz. H arom are the other protons of the 8-mq ligand and the aromatic protons of the PPhMe$_2$, pyridine or 4-Mepy ligands. [c] ν(Pd–Cl) = 288 cm^{-1}; in the corresponding brominated compound, ν(Pd–Br) = 173 cm^{-1} (polyethylene pellets). [d] ν(NO) = 1704 vs and 1682 vs cm^{-1} in KBr pellet; ν(NO) = 1705 vs in THF solution.

is removed under low pressure. The product is extracted from the residue thus obtained with CH_2Cl_2 and is obtained as orange crystals by slow diffusion of hexane into this solution at −20 °C (yield 50%).

Pd(8-mq)COM (M = Mo(CO)$_3$(η-C_5H_5), Co(CO)$_4$) (5d, 5e). To a suspension of 312 mg (1 mmol) of **3d** in 20 mL of THF stirred in an atmosphere of carbon monoxide is added 25 mL of a 0.04 M solution of NaM in THF. A red solution is immediately obtained. After 10 min of stirring, the solvent is removed in vacuo. CO is then readmitted in the flask, and the product is extracted with dichloromethane (50 mL); 50 mL of hexane is slowly added to that solution, and the mixture is cooled to −20 °C. After 2 days, red crystals of **5d** or **5e** are formed (30% yield). These crystals are stable under an atmosphere of nitrogen at −20 °C, but their solutions are only stable for 1 or 2 hours in an atmosphere of CO at room temperature.

X-ray Analysis. Collection and Reduction of the X-ray Data. Single crystals of $C_{26}H_{24}O_3NPMoPd$ (M_r = 631.8) are red-brown, without regular shapes, and are air stable. Preliminary Weissenberg and precession photographs established that the compound crystallizes in the monoclinic space group $P2_1/c$, with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. The unit cell parameters a = 19.807 (3) Å, b = 9.288 (2) Å, c = 14.140 (4) Å, β = 105.41 (3)°, and V = 2508 Å^3 were obtained by least-squares refinement from 25 accurately centered diffractometer reflections by using Mo Kα (λ = 0.70926 Å) graphite-monochromated radiation. The calculated density is 1.67 g cm^{-3} for Z = 4 formula units in the cell. A single crystal of dimensions 0.07 × 0.13 × 0.16 mm was mounted on a Nonius CAD 4 automatic four-circle diffractometer for data collection using the ω–2θ scan technique. The integrated intensities were obtained from scan angles calculated from $\delta = 1.00 + 0.35 \tan \theta$ (in degrees) and increased by 25% at each end for the background count. The crystal-counter distance was 173 mm, and the counter aperture was calculated from $D = 2.00 + 0.50 \tan \theta$ (in millimeters). With the use of the above conditions and graphite-monochromated Mo Kα radiation, the intensities and estimated standard deviations of 4662 reflections were collected in the range $4° < 2\theta < 50°$, with a constant scan rate of 1.6°/min. Three standard reflections were monitored every 200 min of exposure, and no significant variations were observed. All reflections were corrected from Lorentz and polarization effects by the program MAXE.[6] Absorption corrections were not necessary, due to the small dimensions of the crystal and low value of the linear absorption coefficient (μ = 12.8 cm^{-1}) for Mo Kα radiation. Reflections with $\sigma(I)/I > 1$ were rejected, leaving 1899 independent reflections which were used in the structure determination.

Solution and Refinement of the Structure. The coordinates of the heaviest atoms (Pd, Mo, P) as well as those of many of the 33 independent nonhydrogen atoms of the molecule which constitute the asymmetric unit were found with the aid of the program MULTAN[7] in the most probable set. The positions of the remaining atoms were obtained from three-dimensional electron density difference maps. After successive full-matrix least-squares refinement with program SFLS-5,[8] with isotropic and then anisotropic thermal parameters for these 33 atoms, the locations of the 24 independent hydrogen atoms were found on an electron density difference map. They were introduced in the refinement, with isotropic thermal parameters equal to those of the carbon atoms to which they were bonded. Two further cycles of refinement of coordinates and anisotropic thermal parameters of the nonhydrogen atoms, and one last cycle of refinement of coordinates of all atoms, converged to final values of $R = \sum|\Delta F|/\sum|F_o|$ = 0.052 and $R_w = (\sum w(\Delta F)^2/\sum w|F_o|^2)^{1/2}$ = 0.048 with $\Delta F = |F_o| - |F_c|$. The weights were calculated as $1/w = \sigma_F^2 = (\sigma_I^2 + (0.06I)^2)/4T$.[9] Scattering functions were taken from ref 10 with corrections included for both the real and imaginary parts of the anomalous dispersion.[11] No significant peak remained on a final electron density difference map, and no shift greater than 0.1 esd was

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(11) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

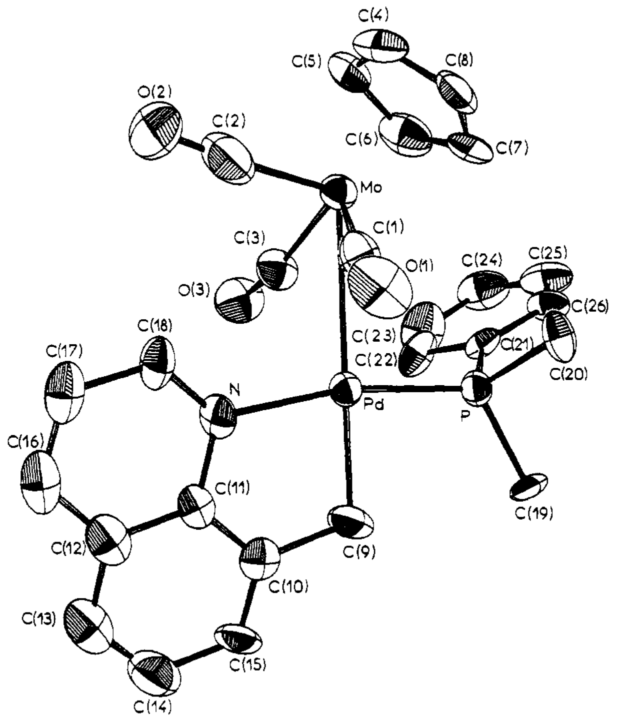

Figure 1. ORTEP drawing of Pd(8-mq)PPhMe$_2$Mo(CO)$_3$(η-C$_5$H$_5$) (**4a**).

observed in the last cycle of refinement.

Results and Discussion

The main difference, that we observed, between the reactivity of compounds of type **1** and that of compounds **3** is that dimetallic species can now be synthesized when a phosphine ligand is attached to the palladium. The behavior of compounds **4** thus obtained is however quite different from the compounds **2** described earlier.[3a] In fact, the reaction between **3c** and NaMo(CO)$_3$(η-C$_5$H$_5$) or NaCo(CO)$_4$ only takes place when hexane is added to the reaction mixture (see Experimental Section). Furthermore, once the compounds **4a** and **4b** are isolated, the Pd–Mo or the Pd–Co bond can be easily broken by adding sodium chloride into a THF solution of **4a** or **4b**. The starting materials **3c** and NaM are regenerated. These observations strongly suggest that the interactions between the palladium and the carbonylmetalate fragments are of an ionic type. The spectroscopic data (Table I) are of little help in determining whether the M moiety is in the position trans to the σ-bonded carbon or to the nitrogen of the cyclopalladated ligand in these compounds. To solve that important question and to get more informations about the nature of the interaction between the two metals, we have undertaken a crystal structure determination of **4a**.

The crystal structure consists of discrete monomeric molecular units of [Pd(8-mq)PPhMe$_2$Mo(CO)$_3$(η-C$_5$H$_5$)] (**4a**). The atomic numbering scheme and a view of the molecule are shown in Figure 1. Relevant bond lengths and angles are listed in Table II. Table III contains the shortest intermolecular distances and Table IV a selection of least-squares planes (supplementary material). Table V gives positional parameters (main text); anisotropic thermal parameters and hydrogen atom parameters are given in the supplementary material in Table VI.

Table II. Relevant Bond Lengths (A) and Angles (Deg) with Their Esd's

Pd–Mo	3.059 (1)	Mo–C(6)	2.383 (11)
Pd–P	2.243 (2)	Mo–C(7)	2.403 (10)
Pd–C(9)	2.074 (12)	Mo–C(8)	2.374 (10)
Pd–N	2.150 (7)	P–C(19)	1.834 (12)
Pd···C(1)	2.516 (12)	P–C(20)	1.832 (12)
Pd···C(3)	2.550 (13)	P–C(21)	1.843 (11)
Mo–C(1)	1.973 (12)	C(1)–O(1)	1.167 (15)
Mo–C(2)	1.922 (13)	C(2)–O(2)	1.173 (16)
Mo–C(3)	1.948 (12)	C(3)–O(3)	1.177 (15)
Mo–C(4)	2.335 (11)	C(9)–C(10)	1.514 (14)
Mo–C(5)	2.346 (12)	C(18)–N	1.306 (15)
		N–C(11)	1.414 (13)

mean C–C dist
- Cp ring 1.413 (19)
- Ph ring 1.381 (17)
- quinoline ring 1.396 (16)

Mo–Pd–P	91.8 (0.1)	Pd–P–C(20)	113.1 (0.3)
Mo–Pd–N	99.2 (0.2)	Pd–P–C(21)	115.2 (0.3)
Mo–Pd–C(9)	175.0 (0.2)	C(19)–P–C(20)	99.8 (0.5)
P–Pd–N	168.7 (0.3)	C(19)–P–C(21)	98.7 (0.5)
P–Pd–C(9)	87.2 (0.3)	C(20)–P–C(21)	108.5 (0.5)
C(9)–Pd–N	82.0 (0.4)	Mo–C(1)–O(1)	168.7 (0.5)
Pd–Mo–C(1)	55.0 (0.2)	Mo–C(2)–O(2)	175.1 (0.6)
Pd–Mo–C(2)	105.0 (0.3)	Mo–C(3)–O(3)	168.1 (0.7)
Pd–Mo–C(3)	56.1 (0.2)	Pd–C(9)–C(10)	109.6 (0.8)
C(1)–Mo–C(2)	87.4 (0.5)	C(18)–N–Pd	130.7 (0.5)
C(1)–Mo–C(3)	105.4 (0.5)	C(11)–N–Pd	111.0 (0.6)
C(2)–Mo–C(3)	85.4 (0.6)	P–C(21)–C(22)	117.1 (0.8)
Pd–P–C(19)	119.5 (0.3)	P–C(21)–C(26)	124.0 (0.7)

mean C–C–C angles
- Cp ring 108.0 (10)
- Ph ring 120.0 (9)
- quinoline ring 119.8 (9)

Table V. Atomic Coordinates (×10^4) for Compound 4a

atom	x	y	z
Pd	1983.7 (0.5)	3938.8 (1.0)	2031.8 (0.6)
Mo	2961.4 (0.6)	65.02 (1.2)	2719.7 (0.7)
P	2511 (2)	2658 (4)	3369 (2)
O(1)	1466 (4)	6422 (11)	3063 (6)
O(2)	2450 (6)	8947 (10)	1214 (7)
O(3)	3098 (5)	4699 (10)	927 (6)
C(1)	2001 (6)	6337 (14)	2865 (8)
C(2)	2616 (8)	7988 (16)	1769 (9)
C(3)	2977 (6)	5303 (14)	1596 (8)
C(4)	3689 (7)	8169 (13)	3740 (9)
C(5)	4097 (7)	7463 (14)	3201 (9)
C(6)	4155 (6)	6006 (16)	3531 (10)
C(7)	3779 (6)	5841 (14)	4241 (8)
C(8)	3483 (7)	7198 (15)	4368 (8)
C(9)	1392 (6)	2117 (14)	1526 (8)
C(10)	972 (6)	2347 (13)	474 (8)
C(11)	913 (5)	3769 (13)	117 (7)
C(12)	470 (6)	4132 (15)	−814 (8)
C(13)	110 (6)	2998 (17)	−1400 (8)
C(14)	192 (7)	1609 (17)	−1061 (9)
C(15)	635 (6)	1279 (15)	−135 (8)
C(16)	429 (6)	5568 (16)	−1133 (8)
C(17)	813 (6)	6592 (15)	−532 (8)
C(18)	1254 (6)	6173 (14)	393 (8)
N	1320 (4)	4847 (11)	711 (6)
C(19)	2200 (6)	835 (13)	3521 (8)
C(20)	2432 (7)	3480 (15)	4512 (8)
C(21)	3441 (6)	2238 (12)	3499 (8)
C(22)	3645 (6)	2029 (14)	2635 (9)
C(23)	4311 (8)	1620 (18)	2679 (10)
C(24)	4813 (7)	1519 (16)	3580 (11)
C(25)	4613 (6)	1731 (15)	4434 (15)
C(26)	3935 (6)	2075 (13)	4391 (8)

The coordination plane of the palladium is nearly planar since only C(9) deviates from that plane by 0.18 Å. The Mo(CO)$_3$(η-C$_5$H$_5$) is bond to the palladium atom in the position trans to the σ-bonded carbon of the 8-methylquinoline ligand. The Pd–Mo distance is quite large (3.059 (1) Å) if it is compared to its value in related compounds: 2.846 (1), mean value of [Pd$_2$Mo$_2$(η-C$_5$H$_5$)$_2$(CO)$_6$(PEt$_3$)$_2$][12] and 2.810

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

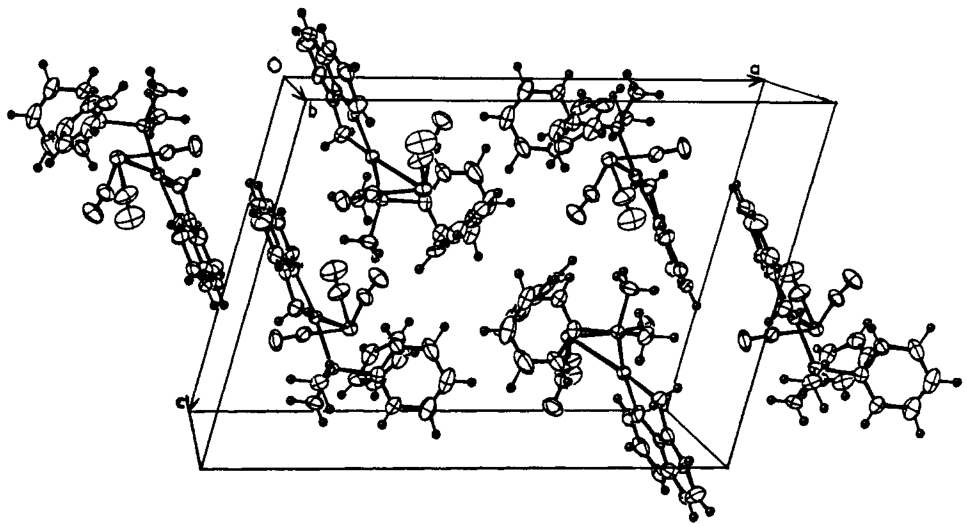

Figure 2. Molecular packing of **4a** within the unit cell.

(1) mean value of $[(\overline{\text{PdNMe}_2\text{CH}_2\text{C}_6\text{H}_4})_2[\mu\text{-}(\text{Mo(CO)}_3(\eta\text{-C}_5\text{H}_5))](\mu\text{-Cl})]$.[13] This value is probably due to the large trans influence of the CH_2 group and could explain the weakness of the Pd–Mo bond which was revealed chemically. Two carbonyl groups are significantly bent (see Table II), giving rise to two short contacts to the palladium atom Pd···C(1) = 2.516 (12) Å and Pd–C(3) = 2.550 (13) Å. Geometrically speaking, these CO groups can be considered as semibridging.[14,15] It is however more reasonable to assign that geometry to steric effects than to electronic redistributions. This has already been suggested recently for some slightly distorted CO groups.[16] The $Mo(CO)_3(\eta\text{-}C_5H_5)$ moiety seems indeed to have adopted the position, relative to the rest of the molecule, which is the less sterically crowded.

The quinoline moiety of the palladated ligand is rigorously planar, and the metallated carbon C(9) deviates from that plane by 0.216 Å. From Figure 2, which shows the arrangment of the molecules in the unit cell, and Table III it can be seen that there is some tendency for two quinoline moieties to make intermolecular contacts (ca. 3.6 Å). This feature has already been observed in our laboratory, in a related molecule.[17]

Compounds **3a** and **3b** react with the carbonylmetalate anion in a similar way to compound **1**.[3] Here we could not verify the same ionic character of the Pd–M bond thus obtained, as in **4a** or **4b**. Thus a different stereochemistry is assigned to compounds **5a**–**5c** (i.e., with the M moiety trans to the nitrogen atom as in compounds **2**[3]).

We have also tested that reaction with the new monomer **3d**, where the ligand is the carbon monoxide. The substitution of the chlorine again takes place, and the reaction resembles the previous ones. Moreover, the chemical shift of the cyclopentadienyl protons for **5d** is the same as that for **5a** and is quite different from that of **4a** (Table I). Thus we tentatively suggest that, for **5d** and **5e**, the M fragment is again bound trans to the nitrogen atom.

In conclusion, this study has revealed several interesting features of the reactivity of the cyclopalladated compounds toward the carbonylmetalate anions. We have now shown that by decreasing the steric hindrance at the position trans to the σ-bonded carbon, the substitution of the chlorine atom by these soft and bulky nucleophiles occurs whatever the ligand coordinated to the palladium is. Because of the limited number of reactions described here, it is difficult to make definitive conclusions about the formation of these dimetallic species. However, we can make the following remarks. An antisymbiotic effect[18] still takes place when the ligand is the pyridine or the carbon monoxide, the soft carbonyl metalate fragment being destabilized trans to the carbon atom and moving trans to the harder one, i.e., the nitrogen. In addition, this study has also shown that this migration cannot take place when a phosphine is bound to the palladium. That ligand shows little tendency to be coordinated trans to the σ-bonded carbon.[19]

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Registry No. **3a**, 79028-47-0; **3b**, 79005-36-0; **3c**, 79005-37-1; **3d**, 79057-86-6; **4a**, 79044-51-2; **4b**, 79005-38-2; **5a**, 79005-39-3; **5b**, 79028-48-1; **5c**, 79005-40-6; **5d**, 79028-49-2; **5e**, 79005-41-7; μ-dichloro-bis(8-methylquinoline-*C*,*N*)dipalladium, 28377-73-3.

Supplementary Material Available: Tables of selected packing distances (Table III), least-squares planes and atomic displacement (Table IV), hydrogen atom coordinates and all temperature factors with esd's (Table VI) and structure amplitudes (Table VII) (10 pages). Ordering information is given on any current masthead page.

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