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Reactivity of Cyclopalladated Compounds. 9.[1] Synthesis of Trinuclear Compounds with a Carbonylmetalate Anion as a Bridging Unit between Two Palladium(II) Centers. Crystal and Molecular Structure of $[(\overline{\mathrm{PdNMe_2CH_2C_6H_4}})_2(\mu\text{-Cl})(\mu\text{-Co(CO)}_4)]$ and $[(\overline{\mathrm{PdNMe_2CH_2C_6H_4}})_2(\mu\text{-Cl})\{\mu\text{-Mo(CO)}_3(\eta^5\text{-C}_5\text{H}_5)\}]$

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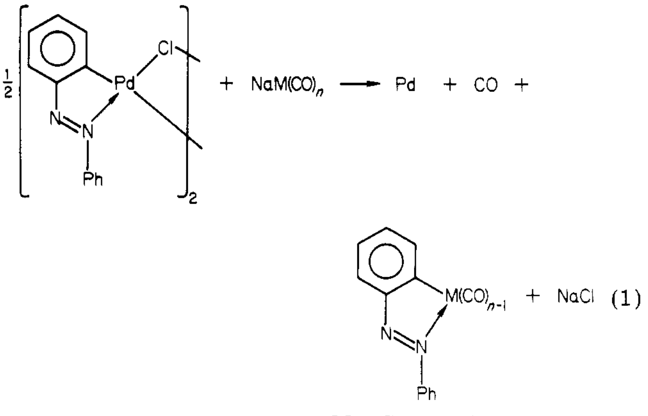
The cyclopalladated dimers of general formula $[\overline{\mathrm{Pd}(\widehat{\mathrm{C\,N}})\mathrm{Cl}}]_2$ (**1a**, $\widehat{\mathrm{C\,N}}$ = dmba, dimethylbenzylamine-C^2,N; **1b**, $\widehat{\mathrm{C\,N}}$ = dmat, 2-(dimethylamino)toluene-C,N; **1c**, $\widehat{\mathrm{C\,N}}$ = 8-mq, 8-methylquinoline-C^8,N) react with carbonylmetalate anions such as $[\mathrm{Co(CO)_4}]^-$, $[\mathrm{Fe(CO)_3NO}]^-$, and $[\mathrm{M(CO)_3Cp}]^-$ (M = Mo, Cr, W) to give trimetallic species where the metalate anion has replaced one bridging chloride in **1**. Two of the resulting compounds were characterized by a single-crystal X-ray diffraction study. Crystals of $[\mathrm{Pd(dmba)}]_2(\mu\text{-Cl})[\mu\text{-Co(CO)}_4]$ (**2a**) belong to the space group Pnma with a = 21.844 (4) Å, b = 11.947 (2) Å, c = 10.754 (2) Å, V = 2806 Å^3, and Z = 4. The structure has been refined to R = 0.024 and R_ω = 0.032. The molecule consists of two Pd(dmba) fragments bridged by a Cl atom and a $\mathrm{Co(CO)_4}$ moiety. The molecule, which has a noncrystallographic mirror of symmetry, may be viewed as an open book structure. The Co atom is located in the trans positions with respect to the N donor atom of the dmba chelates. Two CO groups are semibridging to the Pd atoms. Complex **4a** $[\mathrm{Pd(dmba)}]_2(\mu\text{-Cl})[\mu\text{-Mo(CO)}_3(\eta^5\text{-C}_5\text{H}_5)]$ crystallizes in the space group $P2_1/n$ with a = 20.501 (9) Å, b = 15.624 (6) Å, c = 8.403 (4) Å, β = 99.83 (5)°, V = 2652 Å^3, and Z = 4. The refinement of the structure led to R = 0.040 and R_ω = 0.054. The molecular structure also shows that two cyclopalladated units are held together by a Cl atom and a $\mathrm{Mo(CO)_3Cp}$ moiety. The Pd–Mo bond distances (2.832 (1) and 2.788 (1) Å are in accord with strong metal–metal interactions between these atoms. One CO group is semi triply bridging the $\mathrm{Pd_2Mo}$ triangle whereas the two others are semibridging the Pd–Mo bonds. The degree of symmetry in this molecule is lower than in **2a** since no mirror plane can be found. Here the Cl atom is again located trans to the σ-bonded carbon of the dmba ligands. ^{1}H NMR studies show that both **2a** and **4a** are fluxional molecules in solution. The slow exchange limit of the process can be easily reached for the latter compound. A systematic study on the compounds $[\mathrm{Pd(dmba)}]_2(\mu\text{-Cl})[\mu\text{-W(CO)}_3\mathrm{Cp}]$ (**6a**) and $[\mathrm{Pd(dmat)}]_2(\mu\text{-Cl})[\mu\text{-M(CO)}_3\mathrm{Cp}]$ (**4b**, M = Mo, **5**, M = Cr, and **6b**, M = W) reveals that the ΔG^* value depends only on the nature of the σ-bonded carbon of the $\overline{\mathrm{N\,C}}$ moiety: it is close to 70 kJ mol^{-1} for **4a** and **6a** and close to 50 kJ mol^{-1} for **4b**, **5**, and **6b**. These results allow us to propose a likely mechanism for the exchange process that involves the dissociation of the carbonylmetalate anion from the rest of the molecule.

Introduction

Among the various ways that have been used to synthesize heteropolymetallic complexes the exchange reaction of an halogen by a carbonylmetalate anion has been well investigated[3] and has proven to be a reliable method for obtaining new polynuclear molecules. We have already shown that monomeric cyclopalladated compounds, where the metalate ligand is a tertiary amine, can indeed be used as starting materials to make heterobimetallic complexes containing a Pd–Mo, a Pd–Co, or a Pd–Fe bond.[4] The presence on the palladium atom of a three-electron donor ancillary ligand seemed to stabilize the new molecules thus formed.

That result was in marked contrast to a previous observation by Heck, who reported that the reaction between dimeric cyclopalladated azobenzene and carbonylmetalate anions[5] resulted in the transmetalation reaction shown in eq 1.



M = Co, n = 4
M = Mn, Re, n = 5

We therefore decided to reinvestigate reaction 1 by using dimeric cyclopalladated compounds bearing a $\overline{\mathrm{N\,C}}$ chelate different from azobenzene. Thus, in a preliminary communication[6] we have described the reactions between $[\mathrm{Pd(dmba)Cl}]_2$ (**1a**, dmba = dimethylbenzylamine-C^2,N) and $\mathrm{NaMo(CO)_3(\eta^5\text{-}C_5H_5)}$, $\mathrm{NaCo(CO)_4}$ and $\mathrm{KFe(CO)_3NO}$

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[1] Part 8: Dehand, J.; Mauro, A.; Ossor, H.; Pfeffer, M.; De A. Santos, R. H.; Lechat, J. R. *J. Organomet. Chem.* **1983**, *250*, 537.

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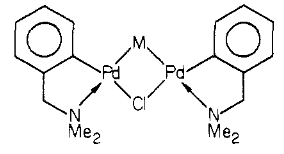
Table I. Selected Spectroscopic Data for Compounds 2-6

	IR data[a] ν(CO), cm^{-1}	^{1}H NMR shifts[b] Cp	NMe$_2$	CH$_2$
[Pd(dmba)]$_2$(μ-Cl)[μ-Co(CO)$_4$] **(2a)**	2018 s, 1963 s 1880 vs, 1860 vs		2.88 (s)	4.08 (s)[c]
[Pd(dmat)]$_2$(μ-Cl)[μ-Co(CO)$_4$] **(2b)**	2016 vs, 1971 s 1883 vs, 1862 vs		3.19 (s)	2.93 (s)
[Pd(8-mq)]$_2$(μ-Cl)[μ-Co(CO)$_4$] **(2c)**	2017 vs, 1968 w, 1882 vs br			3.42 (s)[d]
[Pd(dmba)]$_2$(μ-Cl)[μ-Fe(CO)$_3$NO] **(3)**	1880 vs, 1842 vs[e]		2.85 (s)	4.09 (s)[c]
[Pd(dmba)]$_2$(μ-Cl)[μ-Mo(CO)$_3$Cp] **(4a)**	1844 s, 1770 vs br	5.30 (s)	2.87 (s) 2.68 (s)	4.21 (d) 4.03 (d) $^2J_{HH}$ = 13.3 Hz
[Pd(dmat)]$_2$(μ-Cl)[μ-Mo(CO)$_3$Cp] **(4b)**	1840 s, 1779 vs br	5.33 (s)	3.19 (s)	2.64 (d) 2.58 (d) $^2J_{HH}$ = 13.6 Hz
[Pd(dmat)]$_2$(μ-Cl)[μ-Cr(CO)$_3$Cp] **(5)**	1842 s, 1789 vs, 1769 vs	4.69 (s)	3.20 (s)	2.69 (d) 2.56 (d) $^2J_{HH}$ = 13.2 Hz
[Pd(dmba)]$_2$(μ-Cl)[μ-W(CO)$_3$Cp] **(6a)**	1840 s, 1760 vs br	5.32 (s)	2.75 (s) 2.67 (s)	4.14 (d) 4.01 (d) $^2J_{HH}$ = 13.0 Hz
[Pd(dmat)]$_2$(μ-Cl)[μ-W(CO)$_3$Cp] **(6b)**	1835 s, 1777 vs	5.42 (s)	3.18 (s)	2.67 (s)

[a] In KBr pellets. [b] In ppm in CDCl$_3$ solutions at 20 °C unless otherwise stated. (*s*): singlet, (*d*): doublet. [c] In CD$_2$Cl$_2$ solutions at −20 °C. [d] In CD$_2$Cl$_2$ solutions at 20 °C. [e] ν(NO) = 1740 vs.

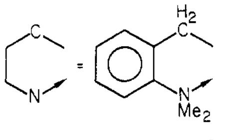
leading to unprecedented trimetallic compounds, as in eq 2.

[Pd(dmba)Cl]$_2$ + NaM ⟶  + NaCl (2)

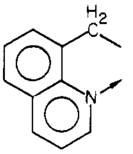
1a

2a, M = Co(CO)$_4$
3, M = Fe(CO)$_3$NO
4a, M = Mo(CO)$_3$Cp

Reaction 2 has now been successfully used with the different $\overline{\text{N C}}$ chelates dmat and 8-mq.



dmat = 2-(dimethylamino)toluene-*C*,*N*



8-mq = 8-methylquinoline-*C*^{8},*N*

In this paper we wish to report these new results and present the full crystal structure data of **2a** and **4a**.

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.[4a,7]

A. Syntheses. Solutions of Na[M(CO)$_3$Cp][8] (M = Cr, Mo, W) and NaCo(CO)$_4$[9] were prepared by Hg/Na reduction of THF solutions of [M(CO)$_3$Cp]$_2$ and Co$_2$(CO)$_8$, respectively. KFe(CO)$_3$NO was prepared according to literature procedure.[10] Complexes [Pd(dmba)Cl]$_2$,[11] [Pd(dmat)Cl]$_2$,[12] and [Pd(8-mq)Cl]$_2$[13] were obtained by literature methods.

A summary of the spectroscopic data (IR and ^{1}H NMR) for all new compounds is given in Table I.

[Pd(dmba)]$_2$(μ-Cl)[μ-Co(CO)$_4$] (2a). A 11-mL sample of a solution of NaCo(CO)$_4$ in THF (0.05 M) was slowly added to a well-stirred solution of [Pd(dmba)Cl]$_2$ (0.276 g, 0.5 mmol) in THF (15 mL) at room temperature. The bright red solution thus obtained was filtered to remove NaCl. *n*-Hexane (40 mL) was slowly added to the filtrate that was then cooled at −20 °C for 24 h. This afforded **2a** as red prisms that were washed with hexane (20 mL) (0.269 g, 78%). Crystals suitable for the X-ray analysis were obtained as a 1:1 solvate of CH$_2$Cl$_2$ by slow diffusion of *n*-pentane in a CH$_2$Cl$_2$ solution of **2a**. Anal. Calcd for C$_{22}$H$_{24}$ClCoN$_2$O$_4$Pd$_2$: C, 38.41; H, 3.49; N, 4.07. Found: C, 38.67; H, 3.36; N, 4.24.

Compound **2b** was prepared by a similar procedure starting with [Pd(dmat)Cl]$_2$ as bright red crystals (50% yield). **2c** was obtained similarly from [Pd(8-mq)Cl]$_2$ as orange crystals (33% yield). Anal. Calcd for C$_{22}$H$_{24}$ClCoN$_2$O$_4$Pd$_2$ (**2b**): C, 38.41; H, 3.49; N, 4.07. Found: C, 38.90; H, 3.38; N, 4.12. Anal. Calcd for C$_{24}$H$_{16}$ClCoN$_2$O$_4$Pd$_2$ (**2c**): C, 40.95; H, 2.27; N, 3.99. Found: C, 40.47; H, 2.37; N, 4.90.

[Pd(dmba)]$_2$(μ-Cl)[μ-Fe(CO)$_3$NO] (3). KFe(CO)$_3$NO (0.230 g, 1.1 mmol) dissolved in THF (20 mL) was added to a suspension of [Pd(dmba)Cl]$_2$ (0.552 g, 1 mmol) in THF (10 mL) affording a red solution after ca. 15 min of stirring at room temperature. This solution was filtered, and *n*-hexane (60 mL) was added. After 48 h at −20 °C bright red crystals were obtained. These crystals were not stable in vacuo because **3** crystallizes with 0.5 mol of THF (600 mg, 82%). Anal. Calcd for C$_{23}$H$_{28}$ClFeN$_3$O$_{4.5}$Pd$_2$: C, 38.21; H, 3.88; N, 5.81. Found: C, 38.00; H, 3.76; N, 6.02.

[Pd(dmba)]$_2$(μ-Cl)[μ-Mo(CO)$_3$Cp] (4a). A 11-mL sample of a solution of NaMo(CO)$_3$Cp in THF (0.05 M) was added to a solution of [Pd(dmba)Cl]$_2$ (0.276 g, 0.5 mmol) in THF (20 mL) at room temperature. This gave a dark red solution that was filtered, and n-hexane (60 mL) was added. After 48 h at −20 °C black crystals of **4a** were obtained (0.266 g, 70%). Crystals suitable for X-ray analysis were grown by slow diffusion of *n*-pentane into a solution of **5a** in CH$_2$Cl$_2$ at −20 °C. Anal. Calcd for C$_{26}$H$_{29}$ClMoN$_2$O$_3$Pd$_2$: C, 40.98; H, 3.81; N, 3.68. Found: C, 41.23; H, 3.70; N, 3.61.

Compound **6a** was prepared by a very similar procedure from a solution of NaW(CO)$_3$Cp. Anal. Calcd for C$_{26}$H$_{29}$ClN$_2$O$_3$Pd$_2$W: C, 36.74; H, 3.41; N, 3.30. Found: C, 37.10; H, 3.32; N, 3.14.

[Pd(dmat)]$_2$(μ-Cl)[μ-Mo(CO)$_3$Cp] (4b). This compound was synthesized by a procedure identical with that used for **4a** starting from [Pd(dmat)Cl]$_2$ in 50% yield.

Compounds **5** and **6b** were prepared similarly by using solutions of NaCr(CO)$_3$Cp and NaW(CO)$_3$Cp, respectively. Anal. Calcd for C$_{26}$H$_{29}$ClMoN$_2$O$_3$Pd$_2$ (**4b**): C, 40.98; H, 3.81; N, 3.68. Found:

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(13) Deeming, A. J.; Rothwell, I. P. *J. Organomet. Chem.* **1981**, *205*, 117.

Table II. Crystal Data and Data Collection Parameters of 2a and 4a

	2a $C_{23}H_{26}Cl_3CoN_2O_4Pd_2$	4a $C_{26}H_{29}ClMoN_2O_3Pd_2$
mol wt	772	761
cryst system	orthorhombic	monoclinic
a, Å	21.844 (4)	20.501 (9)
b, Å	11.947 (2)	15.624 (6)
c, Å	10.754 (2)	8.403 (4)
β, deg		99.83 (5)
V, Å^3	2806	2652
Z	4	4
ρ(calcd), g cm^{-3}	1.83	1.90
cryst dimens, mm	sphere *ϕ* = 0.300 ± 0.005	0.040 × 0.040 × 0.320
space group	*Pnma*	*P*2$_1$/*n*
F_{000}	1520	1496
linear abs coeff, cm^{-1}	21.6	19.0
scan type	*θ*/2*θ*	*θ*/2*θ*
scan range, deg	0.85	1.10
scan speed, deg min^{-1}	2	2
θ limits, deg	2/30	2/27.5
no. of independent obsd data	1974	2330
R	0.024	0.040
R_W	0.032	0.054
std error in an observn of unit weight, e	1.092	1.191
fudge factor	0.08	0.08

C, 41.23; H, 3.70; N, 3.62. Anal. Calcd for $C_{26}H_{29}ClCrN_2O_3Pd_2$ (**5**): C, 43.49; H, 4.04; N, 3.90. Found: C, 42.82; H, 3.77; N, 3.81. Anal. Calcd for $C_{26}H_{29}ClN_2O_3Pd_2W$ (**6b**): C, 36.74; H, 3.41; N, 3.30. Found: C, 36.24; H, 3.29; N, 3.18.

X-ray Data Collections and Structures Determinations. A systematic search in reciprocal space using a Philips PW 1100 automatic four-circle diffractometer and precession camera photographs led to the results reported in Table II. The unit cell dimensions and their standard deviations were refined at room temperature (20 ± 2 °C) with Mo Kα radiation (λ = 0.709 30 Å) using 25 carefully selected reflections.

Crystals were sealed in Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained with a Picker four-circle diffractometer controlled by a PDP8/A computer using graphite-monochromated Mo Kα radiation. Intensity data were collected by using the $\theta/2\theta$ scan technique with 10-s stationary background measurements on both sides of the scan. Each reflection was scanned only if in a prescan $\sigma^2(I)/I$ was less than 5.

For both compounds, the intensities of three reflections were monitored throughout the data collection at intervals of 300 measurements; no significant trend appeared.

The raw data collection measurements were converted to intensities by using standard methods on a Univac 1110 computer. The intensities were corrected for Lorentz and polarization factors and absorption effects by using the numerical integration of Busing and Levy[14] for compound **4a** and the tabulated values for spheres[15] for compound **2a**. For **2a** equivalent reflections were averaged. The variance estimated from counting statistic of an integrated intensity was $\sigma^2(I) = \sigma^2(\text{count}) + (pI)^2$ with $p = 0.05$ for **2a** and 0.08 for **4a**. All reflections with I greater than $3\sigma(I)$ were considered observed.

The data sets were transferred to a PDP 11/60 computer, and the structures were solved by using the Enraf-Nonius SDP/V18 package[16] with the heavy-atom method. Hydrogen atoms were introduced, by their computed coordinates with a C–H distance of 0.95 Å and an isotropic thermal parameter of 6 Å^2 but not refined.

The refinement results are given in Table II. Anisotropic thermal parameters for all non-hydrogen atoms as well as a table listing the observed and calculated structure factors amplitudes of the reflections used in the refinement are available as supplementary materials.[17]

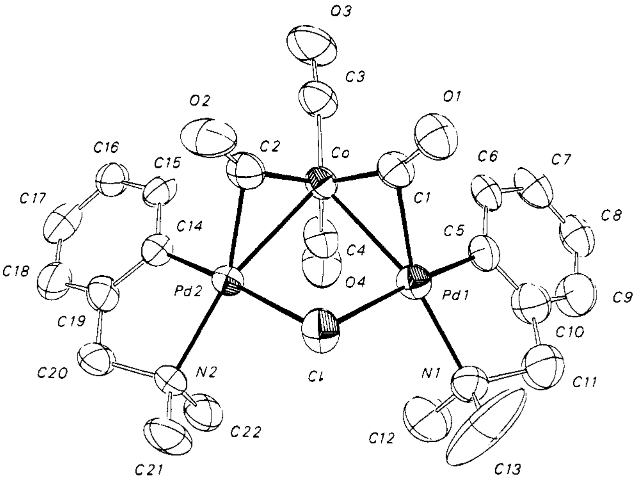

Figure 1. Structure of [Pd(dmba)]$_2$(μ-Cl)(μ-Co(CO)$_4$ (**2a**).

Results and Discussion

Compounds $[\overline{\mathrm{Pd}(\mathrm{C}^\frown\mathrm{N})}]_2(\mu\text{-Cl})[\mu\text{-Co(CO)}_4]$ (2) and $[\overline{\mathrm{Pd}(\mathrm{C}^\frown\mathrm{N})}]_2(\mu\text{-Cl})[\mu\text{-Fe(CO)}_3\mathrm{NO}]$ (3). Solid compound **2a** obtained via reaction 2 is stable at room temperature in an inert atmosphere for several days, but in solution it is stable for only a few hours at −20 °C. It's formula and molecular structure were established by a combination of elemental analysis, IR and ^{1}H NMR spectroscopy, and a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **2a** is shown in Figure 1. Crystal data, the positional coordinates, the interatomic distances and angles, and least-squares planes are given in Tables II, III, IV, and V, respectively.

The most imporant feature of this structure is the Co(CO)$_4$ moiety bridging two palladium atoms. At the time we published our preliminary work on this compound such a bonding mode for this anionic moiety was not known. Since then there has been at least one report by Werner and Thometzek,[18] who published the synthesis of a molecule containing a Pd(I)–Pd(I) moiety bridged by one Co(CO)$_4$ group, but without a crystal structure. **2a** has a

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[14] Busing, W. R.; Lewy, H. A., *Acta Crystallogr., Sect. A* **1957**, *A10*, 180.

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

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Table III. Positional Parameters and Their Estimated Standard Deviations for Compound 2a[a]

atom	x	y	z	B, Å^2
Pd1	0.15229 (2)	0.000	0.07164 (5)	3.453 (9)
Pd2	0.03845 (2)	−0.00616 (7)	0.29289 (4)	3.073 (8)
Co	0.13003 (4)	0.12905 (9)	0.26027 (9)	3.23 (2)
Cl	0.10457 (9)	−0.1455 (2)	0.1969 (2)	4.23 (4)
C1	0.2025 (3)	0.0668 (7)	0.2292 (7)	3.7 (2)
O1	0.2534 (3)	0.0448 (6)	0.2466 (6)	5.3 (1)
C2	0.1115 (4)	0.0583 (7)	0.4041 (8)	4.2 (2)
O2	0.1194 (3)	0.0329 (6)	0.5056 (6)	6.8 (2)
C3	0.1561 (4)	0.2515 (8)	0.331 (1)	4.9 (2)
O3	0.1727 (3)	0.3289 (6)	0.3858 (8)	7.3 (2)
C4	0.0745 (3)	0.1780 (7)	0.1441 (8)	4.3 (2)
O4	0.0428 (3)	0.2126 (7)	0.0761 (6)	6.6 (2)
C5	0.1878 (3)	0.1151 (7)	−0.0423 (7)	3.6 (2)
C6	0.2084 (3)	0.2204 (7)	−0.0120 (7)	3.8 (2)
C7	0.2289 (4)	0.2908 (8)	−0.109 (1)	5.4 (2)
C8	0.2299 (4)	0.2555 (9)	−0.2296 (8)	5.1 (2)
C9	0.2090 (5)	0.152 (1)	−0.2586 (8)	6.0 (2)
C10	0.1901 (5)	0.0813 (8)	−0.1648 (9)	5.3 (2)
C11	0.1822 (6)	−0.0413 (9)	−0.192 (1)	7.0 (3)
N1	0.1391 (3)	−0.0889 (6)	−0.0991 (7)	4.2 (1)
C12	0.0759 (5)	−0.062 (1)	−0.139 (1)	9.3 (4)
C13	0.149 (1)	−0.205 (1)	−0.096 (1)	16.2 (8)
C14	−0.0206 (3)	0.1031 (7)	0.3673 (7)	3.6 (2)
C15	−0.0099 (4)	0.2145 (7)	0.4031 (7)	4.2 (2)
C16	−0.0541 (4)	0.2814 (8)	0.4509 (8)	4.8 (2)
C17	−0.1105 (4)	0.2372 (9)	0.4676 (9)	5.4 (2)
C18	−0.1249 (4)	0.126 (1)	0.4349 (7)	5.3 (2)
C19	−0.0773 (3)	0.0563 (8)	0.3881 (7)	4.0 (2)
C20	−0.0871 (3)	−0.0642 (7)	0.3565 (9)	4.5 (2)
N2	−0.0452 (3)	−0.0945 (6)	0.2559 (7)	3.8 (1)
C21	−0.0411 (4)	−0.2185 (7)	0.251 (1)	5.2 (2)
C22	−0.0690 (4)	−0.0534 (8)	0.1358 (9)	5.4 (2)
C23	0.3676 (8)	0.0614 (9)	−0.255 (1)	9.6 (4)
Cl2	0.3376 (2)	0.0093 (5)	−0.3880 (4)	12.4 (1)
Cl3	0.4432 (2)	0.0093 (5)	−0.2282 (5)	12.5 (1)
H6	0.2086	0.245	0.0721	7
H7	0.2414	0.3663	−0.0891	7
H8	0.2454	0.3044	−0.2922	7
H9	0.2081	0.1268	−0.3432	7
H15	0.0311	0.2444	0.3910	7
H16	−0.0461	0.3577	0.4752	7
H17	−0.1427	0.2830	0.5013	7
H18	−0.1658	0.0965	0.4455	7
H111	0.2219	−0.0786	−0.1855	7
H211	0.1680	−0.0522	−0.2747	7
H120	−0.1287	−0.0759	0.3326	7
H220	−0.0791	−0.1099	0.4288	7
H123	0.3415	0.0381	−0.1848	7
H223	0.3679	0.1400	−0.2564	7
H112	0.0462	−0.0870	−0.0804	7
H212	0.0717	0.0213	−0.1406	7
H312	0.0668	−0.0875	−0.2185	7
H113	0.1274	−0.2438	−0.0351	7
H213	0.1488	−0.2403	−0.1727	7
H313	0.1951	−0.2160	−0.0666	7
H121	−0.0144	−0.2406	0.1838	7
H221	−0.0261	−0.2470	0.3259	7
H321	−0.0808	−0.2493	0.2340	7
H122	−0.0423	−0.0703	0.0698	7
H222	−0.1085	−0.0829	0.1198	7
H322	−0.0731	0.0280	0.1401	7

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

noncrystallographic mirror plane containing cobalt, the chloride ion, and two CO groups (C3O3 and C4O4). The two Pd–Co bond distances are very close to those found in other related polymetallic compounds from our laboratory,[19] suggesting some kind of strong interaction between these metals. Two carbonyl groups (C1O1 and C2O2) are found in typical semibridging positions[20] between the cobalt and the palladium atoms as deduced from both the corresponding Pd–C distances (mean 2.154 Å) and the Co–C–O angles (mean 155.7°). It is therefore reasonable to assign the absorptions at 1880 and 1860 cm^{-1} in the IR spectrum of **2a** to CO stretching modes of these two CO bridging groups. The interaction of two palladium

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(19) Le Borgne, G.; Bouaoud, S. E.; Grandjean, D.; Braunstein, P.; Dehand, J.; Pfeffer, M. *J. Organomet. Chem.* **1977**, *136*, 375.

(20) Curtis, D.; Han, K. R.; Buttler, W. M. *Inorg. Chem.* **1980**, *19*, 2096.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) in [Pd(dmba)$_2$](μ-Cl)[μ-Co(CO)$_4$] (2a)

Bond Distances

Pd1-Pd2	3.442 (1)	N2-C22	1.47 (1)
Pd1-Co	2.594 (1)	C5-C6	1.37 (1)
Pd2-Co	2.595 (1)	C6-C7	1.41 (1)
Pd1-Cl	2.434 (2)	C7-C8	1.36 (1)
Pd2-Cl	2.434 (2)	C8-C9	1.36 (1)
Pd1-C5	1.998 (8)	C9-C10	1.37 (1)
Pd2-C14	2.003 (8)	C10-C5	1.37 (1)
Pd1-N1	2.141 (7)	C14-C15	1.40 (1)
Pd2-N2	2.146 (6)	C15-C16	1.35 (1)
Pd1-C1	2.170 (8)	C16-C17	1.35 (1)
Pd2-C2	2.138 (9)	C17-C18	1.40 (1)
Co-C1	1.780 (8)	C18-C19	1.42 (1)
Co-C2	1.809 (8)	C19-C14	1.37 (1)
Co-C3	1.74 (1)	C10-C11	1.50 (1)
Co-C4	1.83 (1)	C19-C20	1.49 (1)
N1-C11	1.48 (1)	C1-O1	1.15 (1)
N2-C20	1.46 (1)	C2-O2	1.14 (1)
N1-C12	1.47 (1)	C3-O3	1.15 (1)
N1-C13	1.40 (1)	C4-O4	1.08 (1)
N2-C21	1.48 (1)		

Bond Angles

Co-Pd1-Cl	84.9 (1)	Pd2-N2-C20	105.9 (3)
Co-Pd2-Cl	84.9 (1)	N2-Pd2-C14	81.1 (3)
Pd1-Co-Pd2	83.13 (6)	Pd1-C5-C10	113.4 (7)
Pd1-Cl-Pd2	90.01 (1)	Pd2-C14-C19	112.3 (7)
Pd1-C1-Co	81.4 (3)	C5-C10-C11	118 (1)
Pd2-C2-Co	81.7 (3)	C14-C19-C20	119 (1)
C1-Co-C2	99.4 (4)	C10-C11-N1	108 (1)
C3-Co-C4	104.3 (5)	C19-C20-N2	108 (1)
C2-Co-C3	95.2 (4)	Pd1-C1-O1	121.9 (7)
C2-Co-C4	125.6 (4)	Co-C1-O1	156.6 (8)
C1-Co-C3	98.1 (4)	Pd2-C2-O2	123.4 (6)
C1-Co-C4	126.3 (4)	Co-C2-O2	154.8 (7)
N1-Pd1-C5	82.4 (3)	Co-C3-O3	175 (1)
Pd1-N1-C11	107.6 (3)	Co-C4-O4	176 (1)
		mean C-C-C Ph rings	119.9 (3)

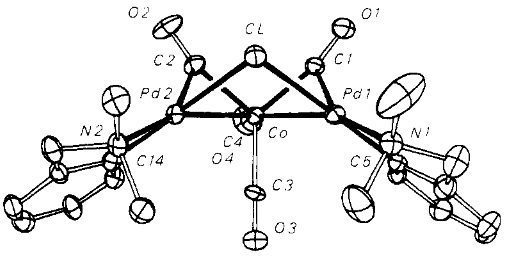

Figure 2. Structure of **2a** viewed along the Co–centroid Pd$_2$Co triangle axis.

Table V. Least-Squares Planes for [Pd(dmba)]$_2$(μ-Cl)[μ-Co(CO)$_4$] (2a)

plane no.	atoms	dist from plane, Å
1	Pd1	−0.005 (1)
	Cl	0.005 (2)
	Co	0.011 (1)
	N1	0.709 (7)
	C5	0.092 (7)
2	Pd1	0.000 (1)
	C5	0.055 (7)
	C10	0.058 (10)
	C11	−0.329 (12)
	N1	0.126 (7)
3	Pd2	−0.012 (1)
	Cl	0.003 (2)
	Co	0.013 (1)
	N2	0.719 (7)
	C14	0.040 (7)
4	Pd2	−0.001 (1)
	C14	0.181 (7)
	C19	−0.012 (8)
	C20	−0.341 (9)
	N2	0.233 (7)
5	Cl	−0.002 (2)
	Co	0.002 (1)
	C3	−0.077 (9)
	C4	−0.017 (8)
	C1[a]	1.369 (7)
	C2[a]	−1.368 (8)
	Pd1[a]	1.714 (1)
	Pd2[a]	−1.729 (1)
6	C5	0.009 (7)
	C6	−0.005 (7)
	C7	0.004 (9)
	C8	−0.008 (9)
	C9	0.117 (10)
	C10	−0.020 (10)
	C11[a]	−0.340 (13)
	N1[a]	0.209 (7)
	Pd1[a]	0.093 (1)
7	C14	0.021 (7)
	C15	−0.010 (8)
	C16	−0.002 (8)
	C17	−0.002 (9)
	C18	0.021 (8)
	C19	0.026 (8)
	C20[a]	−0.074 (9)
	N2[a]	0.580 (7)
	Pd2[a]	0.046 (1)

Dihedral Angles between the Planes

planes	angle, deg	planes	angle, deg
1-2	16.1	4-7	10.9
1-3	44.3	1-5	112.6
3-4	14.8	3-5	68.3
2-6	4.0	6-7	63.0

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

plane	A	B	C	D
1	−0.8937	0.2332	−0.3834	−3.2632
2	−0.9004	0.4041	−0.1613	−3.1193
3	−0.3477	0.2498	−0.9037	−3.1449
4	−0.2080	0.4627	−0.8618	−2.9216
5	0.7290	0.0196	−0.6842	0.1842
6	−0.9276	0.3530	−0.1219	−3.2733
7	−0.2590	0.2893	−0.9215	−3.1877

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

atoms with the cobalt center produces a dramatic effect upon the geometry of the carbonyl groups around the metal. The cobalt atom has a distorted tetrahedral geometry as evidenced by the values of the C–Co–C angles; two of them are close to 100° whereas the two others are close to 125°, allowing the Pd atoms to interact with the cobalt. The Pd1–Pd2 separation (3.442 (1) Å) excludes any interaction between these two metals, this being consistent with their description as Pd(II) centers. The large Pd–Cl bond distances (2.434 (2) Å) are due to the fact that this atom is located trans to two σ-bonded carbons that are known to have a large trans influence.[21] The Pd–N bond distances are close to what was found in a related compound where a Co(CO)$_4$ was bound to Pd trans to nitrogen.[19] The puckering of the cyclometallic rings is a classical feature for cyclometalated benzylamines:[7,22] planes 2 and 4 in Table V both show that the benzylic carbon is at a significantly great distance from the best planes of the metallocycles.

The coordination planes of the Pd atoms (plane 1 and 3, Table V) make a dihedral angle of 44.3°. Thus the

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[21] Dehand, J.; Fischer, J.; Pfeffer, M.; Mitschler, A.; Zinsius, M. *Inorg. Chem.* **1976**, *15*, 2675.

[22] Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J. *Organometallics* **1983**, *2*, 1410.

molecule is best described as an open-book structure. This is shown in an other view of the molecule represented in Figure 2.

Surprisingly, the two protons of the CH_2 groups and the two methyls of the NMe_2 moieties, which are obviously diastereotopic as shown in Figure 2, give rise to one single resonance for the CH_2 protons and another one for the methyls. Even at −100 °C in a CD_2Cl_2 solution no line broadening of these resonances could be detected. This suggests a very rapid fluxional process that creates an averaged plane of symmetry for this molecule (this point will be discussed in more detail in the case of compounds **4**–**6**).

A reaction identical with reaction **2** has now been observed with different cyclopalladated dimers. Thus compounds **1b** and **1c**, where the $\overline{\mathrm{N\;C}}$ chelate is dmat (2-(dimethylamino)toluene-*C*,*N*) and 8-mq (8-methylquinoline-*C*^{8},*N*), respectively, also give rise to heterotrimetallic species **2b** and **2c** when they are allowed to react with $NaCo(CO)_4$. The analytical and spectroscopic data are consistent with a molecular structure that is similar to that of **2a**, i.e., with a $Co(CO)_4$ and a Cl bridging two palladium atoms.

We have indeed checked that in the case of cyclopalladated compounds where the $\overline{\mathrm{C\;N}}$ is orthopalladated azobenzene ($[Pd(Azb)Cl]_2$), no trimetallic complexes could be obtained, even if the correct stoichiometry is used for the reaction (i.e., a Pd:Co ratio of 2:1). In all cases we noticed only the formation of metallic palladium, which confirmed that the transmetalation occurred as in reaction 1.[5] This behavior is likely related to the fact that $[Pd(Azb)Cl]_2$ is easier to reduce than **1a**, **1b**, or **1c**, which was confirmed by electrochemical measurements.[23]

Compound **1a** also reacts with $Fe(CO)_3NO^-$ (isoelectronic to $Co(CO)_4^-$) to give compound **3** in high yield. However, **3** is much less stable than **2a**; it is stable only for several days in the solid state at −20 °C in an inert atmosphere, and in a $CDCl_3$ solution it decomposes even at −20 °C in argon after ca. 30 min. We could not obtain crystals of sufficiently good quality for an X-ray analysis. It is nevertheless reasonable to assign to **3** a molecular structure in which the $Fe(CO)_3NO$ bridges two Pd atoms on the bases of its analytical and spectroscopic data. It is likely that the CO groups in some fashion bridge the Fe and the Pd atoms in this compounds, because the $\nu(C{\equiv}O)$ values in the IR spectra are significantly lower than those of a related compound where the $Fe(CO)_3NO$ moiety was bound to only one Pd atom trans to the nitrogen of a $\mathrm{N}\frown\mathrm{C}$ chelate.[4b]

Compounds $[\overline{\mathrm{Pd(C\frown N)}}]_2(\mu\text{-Cl})[\mu\text{-M(CO)}_3\mathrm{Cp}]$ (M = Mo, Cr, W; 4–6). The exchange process of a bridged chloride ion in **1a** was again observed in the case of $[Mo(CO)_3Cp]^-$, affording **4a**. In order to get a better understanding of the fluxional behavior of this molecule (see below), we have also synthesized compound **6a** by the reaction of **1a** and $[W(CO)_3Cp]^-$ and **4b**, **5**, and **6b** by the reaction of $[Pd(dmat)Cl]_2$ (**1b**) with $[M(CO)_3Cp]^-$, M being Mo, Cr, and W, respectively. All these compounds are rather stable molecule; they can be stored in air at room temperature as crystalline solids for several days, and their solutions are stable for hours in an inert atmosphere at room temperature.

The formulation of **4b**, **5**, **6a**, and **6b** was supported by the great analogy of their spectroscopic data with that of **4a**, which was characterized by an X-ray diffraction study.

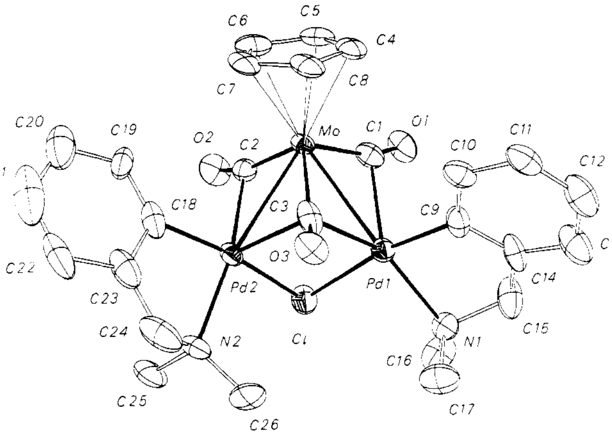

Figure 3. Structure of $[Pd(dmba)]_2(\mu\text{-Cl})(\mu\text{-Mo(CO)}_3Cp)$ (**4a**).

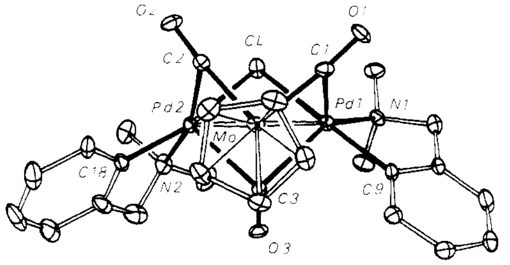

Figure 4. Structure of **4a** viewed along the Mo–centroid Pd_2Mo triangle axis.

The molecular structure of **4a** is shown in Figure 3, crystal data are given in Table II, the positional coordinates in Table VI, the interatomic distances and angles in Table VII, and least-squares planes in Table VIII.

This molecule can be viewed as an arrangement of two Pd atoms bridged by an $Mo(CO)_3Cp$ moiety and a chloride ion. The coordination around each Pd atom is completed by a dmba chelate, in which the σ-bonded carbons are trans to Cl. The degree of symmetry of **4a** is, however, lower than it is in **2a** because the metallocyclic moieties are quite different from one another with respect to the Pd_2MoCl skeleton. The difference is evidenced by the dihedral angles between the best planes of the metallocyclic moieties and the coordination planes of the Pd atoms (see Table VIII). This phenomenon can be seen in the second view of the molecule represented in Figure 4.

The molybdenum atom is bonded to each palladium atom, the Pd–Mo distances being in the range of (or even slightly shorter than) those found previously in the $Pd_2Mo_2Cp_2(\mu_3\text{-CO})_2(\mu\text{-CO})_4(PEt_3)_2$ cluster[24] (abreviated Pd_2Mo_2), where Pd–Mo = 2.827 (1) and 2.864 (1) Å, respectively. As in Pd_2Mo_2, two of the carbonyl groups are semibridged between the Mo and the Pd atoms whereas the third one is assymmetrically bridging over the Pd_2Mo triangle. The Pd–C separations for the semibridging CO (mean 2.24 Å) are significantly shorter as compared to the corresponding CO groups in Pd_2Mo_2[24] (mean 2.41 Å), but the Pd–C distances for the triply bridging CO (mean 2.38 Å) are slightly longer than in Pd_2Mo_2 (mean 2.34 Å). The Mo–C–O angles do not vary significantly from each other (mean 162°) whereas in Pd_2Mo_2 the Mo–C–O angle of triply bridging CO is much smaller than the others. Apparently, the interaction betwen the Pd atoms and the CO groups is similar in both **4a** and Pd_2Mo_2 because the $\nu(C{\equiv}O)$ values in their IR spectra are almost identical.[24]

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[23] Lemoine, P., private communication.

[24] (a) Bender, R.; Braunstein, P.; Dusausoy, Y.; Protas, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 596. (b) Bender R.; Braunstein, P.; Jud, J. M.; Dusausoy, Y. *Inorg. Chem.* **1983**, *22*, 3394.

Table VI. Positional Parameters and Their Estimated Standard Deviations for Compound 4a[a]

atom	x	y	z	B, Å^2
Pd1	0.01885 (4)	0.29393 (6)	0.5367 (1)	2.36 (2)
Pd2	0.16143 (4)	0.23215 (6)	0.4616 (1)	2.20 (2)
Mo	0.03982 (4)	0.18495 (5)	0.2808 (1)	1.87 (2)
Cl	0.1206 (2)	0.3749 (2)	0.5170 (4)	3.53 (7)
C1	-0.0179 (6)	0.2874 (7)	0.265 (1)	2.8 (2)
O1	-0.0555 (4)	0.3396 (5)	0.216 (1)	3.7 (2)
C2	0.1105 (6)	0.2544 (7)	0.212 (1)	2.5 (2)
O2	0.1427 (4)	0.2906 (6)	0.135 (1)	3.9 (2)
C3	0.0683 (5)	0.1562 (7)	0.521 (2)	2.9 (2)
O3	0.0791 (4)	0.1194 (5)	0.639 (1)	3.2 (2)
C4	-0.0496 (6)	0.1001 (7)	0.170 (2)	3.2 (3)
C5	-0.0266 (7)	0.1399 (8)	0.044 (2)	3.4 (3)
C6	0.0365 (7)	0.1110 (8)	0.039 (2)	3.7 (3)
C7	0.0521 (6)	0.0508 (7)	0.164 (2)	3.3 (3)
C8	-0.0018 (6)	0.0444 (7)	0.242 (2)	3.2 (3)
C9	-0.0625 (5)	0.2384 (8)	0.588 (1)	2.9 (2)
C10	-0.0841 (6)	0.1542 (8)	0.555 (2)	3.1 (3)
C11	-0.1413 (6)	0.1248 (9)	0.608 (2)	3.6 (3)
C12	-0.1751 (6)	0.177 (1)	0.693 (2)	4.6 (3)
C13	-0.1540 (6)	0.260 (1)	0.732 (2)	4.5 (3)
C14	-0.0988 (5)	0.2889 (8)	0.672 (2)	3.4 (3)
C15	-0.0751 (7)	0.378 (1)	0.708 (2)	4.6 (3)
N1	-0.0021 (5)	0.3823 (6)	0.718 (1)	2.8 (2)
C16	0.0180 (8)	0.4734 (8)	0.713 (2)	4.1 (3)
C17	0.0295 (8)	0.348 (1)	0.876 (2)	4.3 (3)
C18	0.2104 (6)	0.1297 (8)	0.405 (2)	3.4 (3)
C19	0.2132 (6)	0.0980 (8)	0.255 (2)	3.4 (3)
C20	0.2567 (7)	0.032 (1)	0.237 (2)	5.5 (4)
C21	0.2975 (8)	-0.0005 (9)	0.372 (3)	7.7 (6)
C22	0.2956 (7)	0.029 (1)	0.520 (2)	5.3 (4)
C23	0.2517 (6)	0.0950 (9)	0.542 (2)	4.2 (3)
C24	0.2499 (7)	0.134 (1)	0.700 (2)	5.3 (4)
N2	0.2339 (5)	0.2271 (8)	0.680 (1)	3.5 (2)
C25	0.2942 (6)	0.274 (1)	0.665 (2)	4.7 (3)
C26	0.2098 (7)	0.258 (1)	0.824 (2)	5.4 (4)
HC10	-0.0588	0.1156	0.4951	5
HC11	-0.1570	0.0666	0.5832	5
HC12	-0.2152	0.1568	0.7264	5
HC13	-0.1759	0.2944	0.8015	5
H1C15	-0.0883	0.3973	0.8061	5
H2C15	-0.0967	0.4154	0.6222	5
H1C16	0.0646	0.4786	0.7191	5
H2C16	-0.0031	0.4987	0.6125	5
H3C16	0.0047	0.5049	0.7991	5
H1C17	0.0765	0.3492	0.8867	5
H2C17	0.0169	0.3809	0.9621	5
H3C17	0.0159	0.2899	0.8879	5
HC4	-0.0923	0.1099	0.1978	5
HC5	-0.0516	0.1801	-0.0282	5
HC6	0.0642	0.1295	-0.0372	5
HC7	0.0931	0.0195	0.1895	5
HC8	-0.0047	0.0080	0.3345	5
HC19	0.1851	0.1232	0.1615	5
HC20	0.2567	0.0087	0.1262	5
HC21	0.3283	-0.0446	0.3561	5
HC22	0.3243	0.0022	0.6152	5
H1C24	0.2910	0.1258	0.7721	5
H2C24	0.2158	0.1059	0.7511	5
H1C25	0.2856	0.3325	0.6502	5
H2C25	0.3268	0.2651	0.7599	5
H3C25	0.3119	0.2517	0.5743	5
H1C26	0.1993	0.3175	0.8140	5
H2C26	0.1705	0.2274	0.8375	5
H3C26	0.2423	0.2496	0.9183	5

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

Despite the presence of a triply bridging carbonyl group the Pd1–Pd2 separation (3.241 (1) Å) though much shorter than it is in **2a** here excludes also any kind of Pd···Pd interaction. It is noteworthy that in the Pd_2Mo_2 compounds the Pd–Pd bond distance (2.582 (1) Å) provides a good argument for the description of these metals as Pd(I) centers.[24]

The geometry around the Mo atom resembles, however, that described in the Pd_2Mo_2 cluster, i.e., a three-legged piano stool structure with two extra Pd atoms located within the $Mo(CO)_3$ cone. This argument is supported by the three values of the C–Mo–C angles that are comparable to those in Pd_2Mo_2: two of them are close to 108° and the third one is 89.7 (4)°. the η^5-cyclopentadienyl ligand is at

Table VII. Selected Interatomic Distances (Å) and Angles (deg) in $[Pd(dmba)]_2(\mu\text{-}Cl)[\mu\text{-}Mo(CO)_3Cp]$ (4a)

Bond Distances

Pd1-Pd2	3.241 (1)	N1-C17	1.47 (1)
Pd1-Mo	2.832 (1)	C18-C19	1.36 (1)
Pd2-Mo	2.788 (1)	C19-C20	1.39 (2)
Pd1-Cl	2.470 (3)	C20-C21	1.38 (2)
Pd2-Cl	2.454 (3)	C21-C22	1.33 (3)
Pd1-C9	1.99 (1)	C22-C23	1.40 (2)
Pd2-C18	1.99 (1)	C23-C24	1.47 (2)
Pd1-N1	2.15 (1)	C24-N2	1.49 (2)
Pd2-N2	2.15 (1)	N2-C25	1.46 (2)
Pd1-C1	2.28 (1)	N2-C26	1.46 (2)
Pd1-C3	2.39 (1)	Mo-C4	2.32 (1)
Pd2-C2	2.20 (1)	Mo-C5	2.32 (1)
Pd2-C3	2.37 (1)	Mo-C6	2.33 (1)
Mo-C1	1.98 (1)	Mo-C7	2.34 (1)
Mo-C2	1.97 (1)	Mo-C8	2.35 (1)
Mo-C3	2.05 (1)	C1-O1	1.15 (1)
C9-C10	1.40 (1)	C2-O2	1.14 (1)
C10-C11	1.40 (1)	C3-O3	1.13 (1)
C11-C12	1.35 (2)	C4-C5	1.38 (1)
C12-C13	1.38 (2)	C5-C6	1.38 (1)
C13-C14	1.39 (1)	C6-C7	1.41 (1)
C14-C15	1.49 (2)	C7-C8	1.38 (1)
C15-N1	1.48 (1)	C8-C4	1.37 (1)
N1-C16	1.48 (1)		

Bond Angles

Pd1-Cl-Pd2	82.32 (9)	C1-Mo-C3	108.0 (4)
Pd1-Mo-Pd2	70.43 (3)	Mo-C1-O1	162 (1)
Pd1-C1-O1	114 (1)	Mo-C2-O2	163 (1)
Pd1-C3-O3	115.4 (9)	Mo-C3-O3	161 (1)
Pd2-C2-O2	112.7 (8)	Pd1-C1-Mo	82.9 (4)
Pd2-C3-O3	113.1 (8)	Pd1-C3-Pd2	85.7 (3)
Mo-Pd1-Cl	91.00 (8)	Pd2-C2-Mo	83.5 (4)
Mo-Pd1-C9	98.2 (3)	Pd1-C9-C14	114.3 (4)
Mo-Pd1-N1	175.7 (2)	C9-C14-C15	117 (1)
C1-Pd1-C3	88.5 (4)	C14-C15-N1	109 (1)
Mo-Pd2-Cl	92.40 (8)	C15-N1-Pd1	104.5 (4)
Mo-Pd2-C18	95.6 (3)	Pd2-C18-C23	111.9 (4)
Mo-Pd2-N2	151.2 (3)	C18-C23-C24	118 (1)
C9-Pd1-N1	81.4 (4)	C23-C24-N2	110 (1)
C18-Pd2-N2	82.5 (5)	C24-N2-Pd2	103.8 (4)
C1-Mo-C2	89.7 (4)	mean C-C-C Ph rings	119.9 (4)
C2-Mo-C3	108.1 (5)	mean C-C-C Cp ring	108.0 (5)

Table VIII. Least-Squares Planes for $[Pd(dmba)]_2(\mu\text{-}Cl)[\mu\text{-}Mo(CO)_3Cp]$ (4a)

plane no.	atoms	dist from plane, Å
1	Pd1	−0.001 (1)
	Mo	0.001 (1)
	Cl	−0.005 (3)
	C9	−0.082 (12)
	N1	0.156 (10)
	C15[a]	0.803 (15)
2	Pd1	0.001 (1)
	C9	−0.173 (12)
	C14	0.013 (13)
	C15	0.378 (15)
	N1	−0.180 (10)
3	Pd2	0.009 (1)
	Mo	−0.005 (1)
	Cl	0.006 (3)
	C18	0.314 (14)
	N2	−0.988 (10)
	C24[a]	−1.501 (16)
4	Pd2	−0.001 (1)
	C18	0.182 (12)
	C23	−0.014 (14)
	C24	−0.388 (16)
	N2	0.192 (10)
5	C9	−0.003 (12)
	C10	−0.009 (13)
	C11	0.008 (13)
	C12	0.008 (16)
	C13	−0.024 (16)
	C14	0.017 (13)
	Pd1[a]	−0.119 (1)
	C15[a]	0.015 (15)
	N1[a]	−0.674 (10)
6	C18	0.002 (12)
	C19	0.002 (12)
	C20	−0.008 (15)
	C21	0.007 (15)
	C22	0.003 (15)
	C23	−0.005 (14)
	Pd2[a]	0.235 (1)
	C24[a]	0.074 (16)
	N2[a]	0.848 (11)

Dihedral Angles between the Planes

planes	angle, deg	planes	angle, deg
1-2	9.1	1-5	21.0
1-3	55.0	2-6	49.6
3-4	33.9	5-6	90.8

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

plane	*A*	*B*	*C*	*D*
1	−0.4237	0.6208	−0.6596	0.0839
2	−0.3525	0.5320	−0.7699	−0.8439
3	0.4435	0.3502	−0.8250	−0.7181
4	0.7715	0.5163	−0.3717	2.4956
5	0.4273	0.3101	−0.8493	−2.0675
6	0.7324	0.6725	−0.1068	3.7347

[a] This atom was not used in defining the plane.

[b] Orthogonalized coordinates according to: Blow, D. M. *Acta Crystallogr.* **1960**, *13*, 168.

a typical distance from Mo (2.017 Å).

The chloride ion is in a similar situation in this molecule and in **2a**, and the geometry within the metallocyclic rings is also comparable to that of **2a** (see Table VIII).

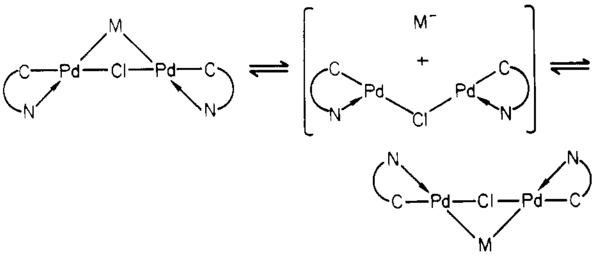
Variable-Temperature ^1H NMR Study of Compounds 4–6. The different roles that the two metallocycles play in the molecular structure of **4a** are probably due to some solid-state interaction because in solution the ^1H NMR spectrum shows no difference between the CH_2 groups or the NMe_2 moieties of the ligands, even at −100 °C in a CD_2Cl_2 solution. However, the important feature of this spectrum is that contrary to what was observed for **2a**, the diastereotopic nature of these protons is now observed; an AB-type pattern is observed for CH_2, and two singlets are observed for the NMe_2 protons. At 30 °C in a benzene-d_6 solution the signal of the NMe_2 coalesces to one single resonance. We could not reach the coalescence of the signal of the CH_2 because it occurs at higher temperature (>60 °C) where **4a** decomposes. We could nevertheless calculate the ΔG^* value for this coalescence (see Table IX). In order to see whether this thermodynamic value is related to the nature of the bridging anions, we have synthesized compound **6a** where the bridging metalate anion is $W(CO)_3Cp$ and **4a′** where the bridging halide is Br. Surprisingly the ΔG^* values obtained for these compounds are very close (within experimental error) to that of **4a**. This result is a strong indication that the process which negates the diastereotopic nature of the NMe_2 group is independent of both the bridging units. We have also synthesized the series of compounds **4b**, **5**, and **6b** where the $\overset{\frown}{\mathrm{C\;N}}$ ancillary ligand is dmat, with the $M(CO)_3Cp$, M = Mo, Cr, and W, respectively. The behavior of these compounds in solution parallels that of **4a** and **6a**, but now the ΔG^* that is calculated from the variable-temperature spectra is significantly lower than it was for those compounds (see Table IX). Thus the ΔG^* value for the rapid exchange process that creates a plane of symmetry for the molecule is dependant only on the nature

Table IX. Free Energies of Activation for the Fluxional Process

compd	solvent	$\Delta\nu$/Hz	T_c/K	$\Delta G^{\ddagger}{}_{T_c}{}^{a}$/ kJ mol^{-1}
4a	[$^2H_8$]toluene	7	330	73.1
	[$^2H_6$]benzene	4	303	68.6
4a′ ^{b}	[$^2H_6$]benzene	6	311	69.4
6a	[$^2H_6$]benzene	14	314	67.9
4b	[^{2}H]chloroform	26.5	237	49.3
	[$^2H_8$]toluene	37.5	241	49.7
5	[^{2}H]chloroform	28.5	241	50.2
6b	[^{2}H]chloroform	28	236	49.3

^{a} Calculated by using the expression $\Delta G^{\ddagger}{}_{T_c} = -RT \ln (\pi \Delta\nu h/(2kT_c)^{1/2})$, where T_c = coalescence temperature and $\Delta\nu$ = chemical shift separation of exchanging nuclei (Kost, D.; Coulson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.*, 1971, 656), the coalescing signals being those of the NMe_2 groups. ^{b} 4a′ = [(Pd(dmba)]$_2$(μ-Br)(μ-Mo(CO)$_3$Cp).

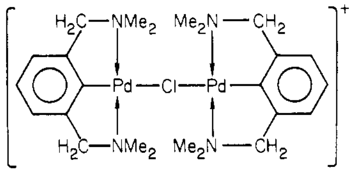
of the σ-bonded carbon atom of the ancillary $\overline{\text{N C}}$ ligand. Among the various pathways that can be invoked for the exchange reaction, we prefer the one that involves an ionic interaction between the ($\overline{\text{N C}}$)Pd)$_2$(μ-Cl) unit and the M(CO)$_3$Cp moiety as described in reaction 3.



(3)

An ionic interaction between the carbonyl metalate fragment and the rest of the molecule is indeed surprising since the M–Pd distances observed for these compounds do not appear unusually long. However, there is some evidence that the ML_n moieties are able to readily dissociate in these trinuclear compounds according to the following experiment: if one treats a solution of compound **2c** in THF by an excess of NaMo(CO)$_3$Cp, one obtains quantitatively the compound [Pd(8-mq)]$_2$(μ-Mo(CO)$_3$Cp)(μ-Cl) described recently[25] that is less soluble than **2c**. Thus in this reaction it is possible to displace the bridging Co(CO)$_4^-$ moiety in **2c** by Mo(CO)$_3$Cp$^-$.

Moreover, our hypothesis is supported by the recent report of the isolation of the related dinuclear cation[26] represented A.



A

In conclusion this work is another demonstration that cyclometalated compounds can be used as interesting starting materials to synthesize compounds with unusual coordination modes. The $\overline{\text{N C}}$ ancillary chelates do indeed confer improved stabilities on the metals to which they are bonded. This has now allowed us to demonstrate conclusively that carbonyl metalate anions can act as bridging units between two Pd(II) centers. These anions may thus be formally considered as four-electron donor ligands in these new molecules, a feature which has been encountered several times with Pd(I) or Pt(I) metals.[18,24,27]

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Registry No. **1a**, 18987-59-2; **2a**, 74989-61-0; **2b**, 91210-66-1; **2c**, 91210-67-2; **3**, 74964-74-2; **4a**, 74981-50-3; **4b**, 91228-87-4; **5**, 91210-68-3; **6a**, 91210-69-4; **6b**, 91210-70-7; [Pd(dmat)Cl]$_2$, 79018-48-7; [Pd(8-mq)Cl]$_2$, 28377-73-3.

Supplementary Material Available: Tables of anisotropic thermal parameters for (Tables SI and SII) and observed and calculated structure factors (Tables SIII and SIV) for **2a** and **4a** (23 pages). Ordering information is given on any current masthead page.

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