transition temperature (54.9 °C)[22] of DSPC, which is in excess of our reaction temperature.

Using model solvent data in Table II, we find a linear relationship between the quantity $(1/a - 1)$ and η, where η is bulk solvent viscosity[26] (Figure 1). The a data for DLPC and DMPC fall on the abscissa to give a bilayer microviscosity equivalent to about 8 cP at 50 °C.

We conclude that free-radical cage escape is depressed in the bilayer system compared with bulk-phase hydrocarbon solvents of the same chain length. Escape is more efficient, however, than predicted by microviscosities measured by probe studies.[16-19] Ester solvents match in polarity but are less viscous than the membrane environment probed by ABCP and BHT. Studies of the effect of bilayer structure on a and on antioxidant reactivities are continuing.

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[26] The competition equation which determines a can be inverted and rearranged to give $1/a - 1 = k_r/k_{diff}$, where k_r is the rate constant for in-cage coupling and k_{diff} is the rate constant for radical diffusion out of the cage. With the assumption of constant k_r, our empirical treatment implies that k_{diff} varies as η^n, where $n = -0.5$, a result similar to that in ref 11.

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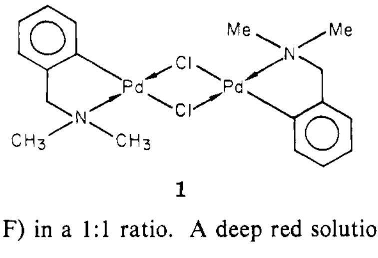
Synthesis of New Heteropolymetallic Compounds with Carbonylmetallate Anions as Bridges between Two Palladium Atoms: X-ray Crystal Structures of $[\{\overline{PdNMe_2CH_2C_6H_4}\}_2\mu\text{-}\{Co(CO)_4\}\mu Cl]$ and $[\{\overline{PdNMe_2CH_2C_6H_4}\}_2\mu\text{-}\{Mo(CO)_3(\eta\text{-}C_5H_5)\}\mu Cl]$

Sir:

Since our discovery of the first stable dimetallic species containing a Pd-Co or a Pd-Mo bond by the reaction of carbonylmetallate anions with monomeric cyclopalladated compounds,[1] we have explored the reaction of these anions with dimeric cyclopalladated species. A related reaction has been used previously[2] to transfer orthometallated azobenzenes on cobalt, manganese, or rhenium carbonyls. Herein we report that by using different cyclopalladated dimers a completely different reaction occurs since this time trimetallic compounds are obtained.

sym-Di-μ-chloro-bis[2-[(dimethylamino)methyl]phenyl]dipalladium **1** suspended in THF reacts quasi-instantaneously at room temperature with $NaMo(CO)_3(\eta\text{-}C_5H_5)$ (2×10^{-2} M solution in THF) in a 1:1 ratio. A deep red solution is obtained from which black crystals are precipitated 1 day after the addition of hexane at -20 °C (70% yield). Microanalytical and spectroscopic data indicate the general formula as $[\{\overline{Pd(NMe_2CH_2C_6H_4)}\}_2\mu\text{-}\{Mo(CO)_3(\eta\text{-}C_5H_5)\}\mu\text{-}Cl]$[3] **2**. In order to establish the geometry of this new type of compound on a firm basis, a single-crystal X-ray-diffraction study was carried out on **2**. Suitable crystals for X-ray study were obtained by slow diffusion of hexane into a dichloromethane solution of **2** at -20 °C. Crystal data[4] for **2** ($Pd_2MoClO_3N_2C_{26}H_{29}$) are the following: $M_r = 761$; monoclinic; space group $P2_1/n$; $a = 20.501(9)$, $b = 15.625(6)$, $c = 8.403(4)$ Å; $\beta = 99.83(5)°$; $V = 2652$ Å^3; $Z = 4$; $d_{obsd} = 1.88$ g/cm^3, $d_{calcd} = 1.90$ g/cm^3, $\mu(\text{Mo K}\alpha) = 19.0$ cm^{-1}. Final $R = 0.040$ ($R' = 0.054$) for 2330 absorption-corrected intensities [293 K, $1.1° < 2\theta < 55°$] with $I > 3\sigma(I)$.



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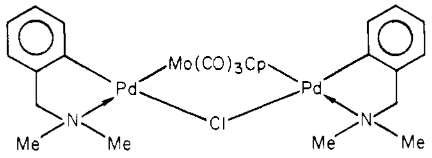

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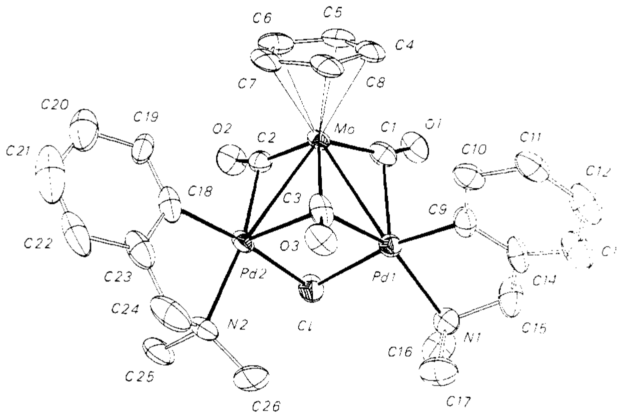

Figure 1. The molecular geometry of $[\{\overline{PdNMe_2CH_2C_6H_4}\}_2\mu\{Mo(CO)_3\eta\text{-}C_5H_5\}\mu Cl]$, including the atomic-numbering scheme. Bond lengths: Pd1-Mo 2.832 (1), Pd2-Mo 2.788 (1), Pd1-Cl 2.470 (3), Pd2-Cl 2.454 (3), Pd1-C1 2.28 (1), Pd1-C3 2.39 (1), Pd2-C2 2.20 (1), Pd2-C3 2.37 (1), Mo-C1 1.98 (1), Mo-C2 1.98 (1), and Mo-C3 2.05 (1) Å. Angles: Pd1-Mo-Pd2 70.43 (3), Pd1-Cl-Pd2 82.32 (9), Mo-C1-O1 1.62 (1), Mo-C2-O2 163 (1), and Mo-C3-O3 161 (1)°.

The molecular structure (Figure 1) reveals that the two palladium atoms are bridged by a chlorine atom and the $Mo(CO)_3(\eta\text{-}C_5H_5)$ moiety. Two of the carbonyl groups are semibridging to the palladium atoms[5] whereas the third one is triply bridging on the Pd_2Mo triangle. The arrangement of the $Mo(CO)_3(\eta\text{-}C_5H_5)$ moiety between the palladium atoms is in fact reminiscent of that found in the heterotetrametallic $Pd_2Mo_2(\eta\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2(\mu_2\text{-}CO)_4(PEt_3)_2$ cluster[6] in which two $Mo(CO)_3(\eta\text{-}C_5H_5)$ groups are bridged between two palladium atoms. In this latter case, however, there was a Pd-Pd bond [Pd-Pd = 2.582 (1) Å] whereas in compound **2** the Pd1-Pd2 distance is 3.241 (1) Å, which excludes, therefore, a metal-metal interaction. The geometry of the metalated ligand is close to what has been found for related compounds.[7] There is no plane of symmetry in the molecule because the two cyclometallated ligands behave

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[1] (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.

[2] Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 313.

[3] Compound **2**: IR ν_{CO} (KBr pellet) 1844 (s), 1770 (vbr s); ν_{PdCl} (polyethylene pellet) 197 cm^{-1}; ^{1}H NMR (250 MHz, CD_2Cl_2) 7.03-6.81 (m, 4 H, C_6H_4), 5.30 (s, 5 H, C_5H_5), 4.21, 4.03 (AB pattern, 2 H, CH_2, J_{HH} = 13.3 Hz), 2.87 (s, 3 H, CH_3), 2.68 ppm (s, 3 H, CH_3).

[4] A Picker four-circle diffractometer was used for both compound **2** and **4** with a monochromated Mo Kα radiation, $\lambda = 0.70930$ Å.

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[7] (a) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490. (b) Little, R. G.; Doedens, R. J. *Inorg. Chem.* **1973**, *12*, 844.

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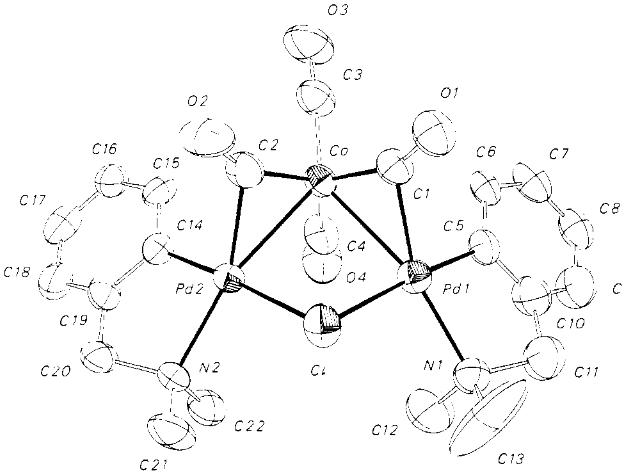
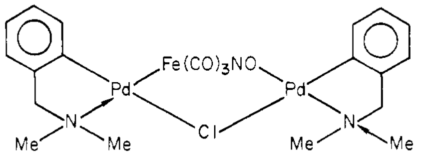


Figure 2. The molecular geometry of $[\{\overline{\mathrm{PdNMe_2CH_2C_6H_4}}\}_2\mu\{\mathrm{Co(CO)_4}\}\mu\mathrm{Cl}]$, including the atomic-numbering scheme. Bond lengths: Pd1–Co 2.597 (1), Pd2–Co 2.595 (1), Pd1–Cl 2.434 (2), Pd2–Cl 2.434 (2), Pd1–C1 2.170 (8), Pd2–C2 2.138 (9), Co–C1 1.780 (8), and Co–C2 1.809 (8) Å. Angles: Pd1–Co–Pd2 83.1 (6), Pd2–Cl–Pd2 90.01 (7), Co–C1–O1 156.6 (8), and Co–C2–O2 154.8 (7)°.

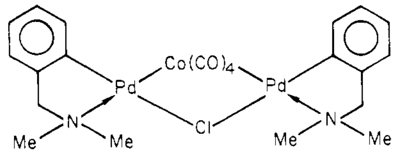
quite differently from each other toward the Pd_2MoCl skeleton.[8] In fact, the inequivalence of the two ligands in the solid state could not be visualized by ^1H NMR in solution because even at −90 °C only one signal for the CH_2 protons and two for the CH_3 protons is found, suggesting that the ligands exchange their role rapidly on the NMR time scale.

The dimeric cyclopalladated compound **1** reacts similarly with $\mathrm{KFe(CO)_3NO}$ to give red crystals of $[\{\overline{\mathrm{Pd(NMe_2CH_2C_6H_4)}}\}_2\mu\text{-}\{\mathrm{Fe(CO)_3NO}\}\mu\text{-}\mathrm{Cl}]$[9] **3** (85% yield). Compound **3** crystallizes with one molecule of THF and is rather unstable since it decomposes even at −20 °C under an inert atmosphere. However, it was possible to get good analytical and spectroscopic data[9] which support the stoichiometry of the compound. Compound **1** reacts also with $\mathrm{NaCo(CO)_4}$ to give red microcrystals of $[\{\overline{\mathrm{Pd(NMe_2CH_2C_6H_4)}}\}_2\mu\text{-}\{\mathrm{Co(CO)_4}\}\mu\text{-}\mathrm{Cl}]$ in 80% yield. This compound is a mixture of compounds **4** and **5**.[10] The cis form of this compound **4** was isolated pure by crystallization from CH_2Cl_2 hexane solution as red prisms and contained one dichloromethane of crystallization. We have not yet been able to isolate compound **5** in pure form.



3

The ^1H NMR spectra of compounds **3** and **4** are surprisingly quite different from that of compound **2** since neither the AB pattern for the CH_2 protons nor the two peaks for the CH_3 protons are observed. We only notice two single absorptions this time in the ratio 1:3 for the CH_2 and CH_3 protons, respectively. We have thus carried out a single-crystal X-ray-diffraction study on compound **4** in order to establish the structural changes due to a different carbonylmetallate anion bridge between the two cyclopalladated moieties. Crystal data for **4** ($Pd_2CoCl_3O_4N_2C_{23}H_{26}$) are the following: $M_r = 772$; orthorhombic; space group *Pnma*; $a = 21.844$ (4), $b = 19.947$ (2), $c = 10.754$ (2) Å; $V = 4686$ Å^3; $Z = 6$; $d_{\mathrm{obsd}} = 1.62$ g/cm^3, $d_{\mathrm{calcd}} = 1.64$ g/cm^3; $\mu(\mathrm{Mo\,K}\alpha) = 19.7$ cm^{-1}. Final $R = 0.024$ ($R' = 0.032$) for 1976 absorption-corrected intensities [293 K, 0.85° $< 2\theta <$ 60°] with $I > 3\sigma(I)$.



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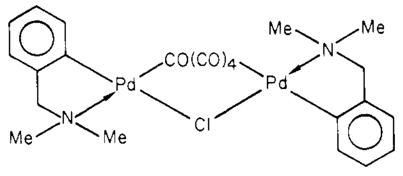

5

The molecular structure (Figure 2) shows that the Pd atoms are indeed bridged by the $Co(CO)_4$ group and by a chlorine atom. The molecule has a noncrystallographic mirror plane containing a $Co(CO)_2$ moiety and the chlorine atom. The coordination planes of the Pd atoms make a dihedral angle of 44.3°. The Pd1–Pd2 distance is significantly longer than that found in compound **2** [Pd1–Pd2 = 3.442 (1) Å]. The Pd–Co distances [2.595 (1) Å] are close to that found in the dimetallic species[1b] [2.604 (1) Å]. This time we only notice two semibridged CO groups, but they are significantly closer to the Pd atoms than they were in the previous case (see Figure 2). In view of the crystal structure which shows that the two protons of the CH_2 group and the methyl of the same ligand are inequivalent, the ^1H NMR spectra of compounds **3** and **4** could only be explained by the fact that these molecules are fluxional in such a way that a plane of symmetry containing Pd1, Pd2, Co, and the cyclometallated ligands is created. The interconversion between the different forms existing in solution must be very fast since even at −100 °C no noticeable change was observed in the spectrum of **4**.

In conclusion, this new class of compounds displays some interesting features. The carbonylmetallate anions are known to behave as one-electron-donor systems.[11] We have now shown that they can also be used as formally three-electron donors, this being achieved by means of a variable number of semibridging carbonyls between the anionic metal and the palladium(II) moieties.

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(8) This observation is demonstrated by the dihedral angles between the best planes defined by P_1 [Pd1 (−0.001 (0.001)), Mo (0.001 (0.001)), Cl (−0.005 (0.003)), C9 (−0.082 (0.012)), N1 (0.156 (0.010))] and P_2 [Pd1 (0.001 (0.001)), C9 (−0.173 (0.012)), C14 (0.013 (0.013)), C15 (0.378 (0.015)), N1 (0.180 (0.010)) = 9.1°] compared to that between the planes P_3 [Pd2 (0.009 (0.001)), Mo (−0.005 (0.001)), Cl (0.006 (0.003)), C18 (0.314 (0.014)), N2 (−0.988 (0.010))] and P_4 [Pd2 (−0.001 (0.001)), C18 (0.182 (0.012)), C23 (−0.014 (0.014)), C24 (−0.388 (0.016)), and N2 (0.192 (0.010)) = 33.9°]. Dihedral angles between P_1 and P_3 = 55°, P_2 and P_4 = 73.2°.

(9) Compound **3**: IR ν_{CO} (Nujol) 1880 (vs), 1842 (vs); ν_{NO} 1740 (vs); ν_{PdCl} (polyethylene pellet) 210 cm^{-1}; ^1H NMR (250 MHz, CD_2Cl_2 −20 °C) 7.00–6.85 (m, 4 H, C_6H_4), 4.09 (s, 2 H, CH_2), 2.85 ppm (s, 6 H, CH_3).

(10) Compounds **4** and **5**: IR ν_{CO} (Nujol) 2018 (s), 1963 (s), 1880 (vs), 1860 (vs); ν_{PdCl} (polyethylene pellet) 204 cm^{-1}; ^1H NMR (250 MHz, CD_2Cl_2, −10 °C) 7.01–6.90 (m, 4 H, C_6H_4); compound **4** 4.08 (s, 2 H, CH_2), 2.88 ppm (s, 6 H, CH_3); compound **5** 3.93 (br s, 2 H, CH_2), 2.83 (s, 3 H, CH_3), and 2.81 ppm (s, 3 H, CH_3).

(11) See, for example: Braunstein, P.; Dehand, J. *Bull. Soc. Chim. Fr.* **1975**, 1997.

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