the crystal is composed of discrete molecules of $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2$ (Figure 1), containing two Zr atoms bonded to two bridging chlorines and η^5-bonded to the cyclopentadienyl rings and bridging fulvalene ligand.

The Zr–Zr distance [3.233 (1) Å] is consistent with the formation of a M–M bond. The coordination around each Zr atom can be described as a distorted tetrahedron if we consider the Cp ring centroid as each occupying one coordination site around the metal.

The fulvalene ligand is folded, forming a dihedral angle of 166.7 (1)° between the two ring planes. The inter-ring bond distance C1–C6 is 1.451 (10) Å, and an almost negligible twist is observed along this bond [dihedral angles C5–C1–C6–C7 = 1.2 (1)°, C2–C1–C6–C10 = 1.4 (1)°]. The angles subtended at the Zr by the centroids of the two staggered individual Cp and fulvalene [(Cp1)–Zr1–(Cp4) = 135.1 (2)°, (Cp2)–Zr2–(Cp3) = 135.4 (4)°; (Cp) = ring centroid], are in the region expected for a normal bent η^5-Cp metal system. Probably as a result of the M–M interaction, the plane containing the Zr_2Cl_2 fragment is symmetrically folded along the Zr–Zr vector [torsion angle Cl1–Zr1–Zr2–Cl2 = 159.0 (1)°], assuming a butterfly configuration with the two bridging chlorine atoms symmetrically placed on the wings. The Zr–Cl–Zr [77.7 (1)–77.6(1)°] and Cl–Zr–Cl [100.5 (1)–99.5 (1)°] angles are comparable to those observed by Schrock for a similar molecular frame.[7] The little increase in Zr–Cl [Zr1–Cl1 = 2.591 (2) Å, Zr2–Cl1 = 2.568 (2) Å, Zr1–Cl2 = 2.583 (2) Å, Zr2–Cl2 = 2.571 (2) Å] and Zr–Zr bond lengths, in this case, can be ascribed to a distortion caused by the fulvalene ligand. The Cl1···Cl2 nonbonded distance [3.950 (3) Å] is just 0.35 Å larger than the van der Waals diameter for Cl. All the other bond lengths and angles are as expected.

The absence of any hydride signal in both the IR and ^{1}H NMR spectra, down to a δ value of −30 ppm, rules out the presence of bridging hydrogen atoms undetected by the X-ray diffraction. The diamagnetism of 1, containing two Zr(III) atoms, can be rationalized either by a direct M–M interaction (bond) or by ligand-propagated superexchange.[15] In the present case, the Zr–Zr distance falls within the range observed for other transition metals with similar arrangement (Table I). Since only few structures of Zr(III) species have been clarified by X-ray analysis (Table II), the evaluation of the significance of a Zr–Zr distance in the complex I is difficult and any extensive comparison with other Zr(III) organometallic derivatives is impossible. It is unclear whether Zr(II) or Zr(III) is responsible for the unexpected formation of fulvalene in reaction 1. Further work to clarify this point is presently in progress together with a broad investigation of the reactivity of complex I.

Acknowledgment. We are indebted to the generosity of Columbia University Chemistry Department for supporting this work.

Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, atomic coordinates, interatomic distances, bond lengths, bond angles, and torsion angles and a stereoview and a lateral view of the molecule (18 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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(14) X-ray diffraction data: crystal size (mm), 0.40 × 0.45 × 0.80, deep red prism; monoclinic, space group $P2_1/n$; a = 8.234 (4) Å, b = 15.199 (5) Å, c = 14.096 (5) Å, β = 93.65 (3)°, Z = 4, V = 1761 Å^3, d(calcd) = 1.93 g/cm^{-3}, μ(Cu) = 131.0 cm^{-1} (absorption coefficient); F(000) = 1008; data were collected on a Nicolet R3m diffractometer; Cu radiation, $\bar{\lambda}$ = 1.541 78 Å; scan mode = $\theta/2\theta$, scan speed = 3.91 −29.3 deg·min^{-1}, scan width = 2.01 −2.44; T = 298 K; measured reflections 2693, range of $hkl = (+h, +k, \pm l)$; $(\sin\theta)/\lambda$ limit (Å^{-1}) = 0.544 ($2\theta_{max}$ = 114°); no. of unique reflections, 2379; no. of reflections used in analysis, 2182 [$I > 3\sigma(I)$]; structure solved by direct method; all the non-hydrogen atoms were located and refined anisotropically; hydrogen atom positions were calculated; number of variables, 217; R = 0.053; R_w = 0.068, $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ with g = 0.0005; GOF = 2.522; largest remaining peak, 1.12 e/Å; largest shift/esd, final cycle, 0.057.

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Influence of the Donor Atom in Metallocyclic Rings on the Insertion of *tert*-Butyl Isocyanide and Carbon Monoxide into Their Pd–C Bonds.[1] X-ray Molecular Structure of $[\overline{\mathrm{Pd}(\eta\text{-}(\mathrm{C,N})\text{-}\mu\text{-}\mathrm{C}(\mathrm{C_6H_4CH_2S}}\mathrm{Me})\!=\!\mathrm{N}\text{-}t\text{-}\mathrm{Bu})\mathrm{Br}]_2$

Jairton Dupont,[2a] Michel Pfeffer,*[2a]
Jean Claude Daran,[2b] and Yves Jeannin[2b]
Laboratoire de Chimie de Coordination, UA 416 du CNRS
Université Louis Pasteur
F-67070 Strasbourg Cêdex, France
Laboratoire de Chimie des Mêtaux de Transition
UA 419 du CNRS, Université Pierre et Marie Curie
F-75230 Paris Cêdex 05, France

Received December 3, 1986

Summary: The insertion of CO and *tert*-butyl isocyanide (*t*-BuNC) into the Pd–C bonds of metallocyclic complexes occurs much more readily with cyclopalladated benzyl methyl sulfide or methyl 1-naphthyl sulfide derivatives than with the corresponding compounds in which the SMe unit is replaced by an NMe_2 group. These reactions afford new compounds containing six-membered organopalladium rings, in both cases the reaction with CO being reversible.

The reaction of nucleophiles and electrophiles with cyclopalladated compounds is well-known to produce new organopalladium compounds or/and organic products.[3a]

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(1) Reactivity of Cyclopalladated Compounds. 17. Part 16: see ref 3i.

(2) (a) Laboratoire de Chimie de Coordination. (b) Laboratoire de Chimie des Mêtaux de Transition.

(3) (a) For a recent review see: Ryabov, A. D. *Synthesis* **1985**, 233. (b) Ossor, H.; Pfeffer, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1540. (c) O'Sullivan, R. D.; Perkins, A. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1165. (d) Massarani, F.; Pfeffer, M.; Le Borgne, G. *J. Chem. Soc., Chem. Commun.* **1986**, 488. (e) Albinati, A.; Pregosin, P. S.; Ruedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046. (f) Barr, N.; Bartley, J. P.; Clark, P. W.; Dunston, P.; Dyke, S. F. *J. Organomet. Chem.* **1986**, *302*, 117. (g) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1986**, *5*, 1922. (h) Dupont, J.; Pfeffer, M. *J. Organomet. Chem.* **1987**, *321*, C13. (i) Massarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics*, in press.

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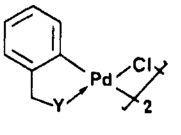
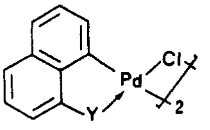
The nature of these products depends on various factors such as the three-electron-donor chelates,[3b–d] the other substituents on the palladium center,[3e–i] and the reaction conditions[3f] (temperature, stoichiometry, etc.). Due to this enormous complexity the rationalization of the different reaction paths becomes somewhat difficult. We have, therefore, decided to investigate to what extent each parameter defining the cyclometalated molecules can influence the course of the reactions. For example we have already demonstrated that changing the substituents on the palladium center modifies dramatically the reactions that a given cyclopalladated compound displays toward alkynes.[3h,i] We now report here some preliminary results that show how the donor atom present in these metallocycles modulates their reactivity toward the insertion of nucleophiles, such as *t*-BuNC or carbon monoxide, into the Pd–C bonds.

We have recently described the synthesis of **1a**,[3h] and we have now successfully obtained compound **2a** starting from methyl 1-naphthyl sulfide[4] following a similar procedure to that used for **1a**. These compounds are closely related to **1b** and **2b**, particularly when considering the steric effect of the SMe vs. the NMe_2 unit.[5] Therefore, the comparison of the chemistry of these two pairs of compounds should provide interesting data with regard to the role that the donor atoms can play during reactions involving the Pd–C bonds.



1a, Y= SMe

1b, Y= NMe_2



2a, Y= SMe

2b, Y= NMe_2

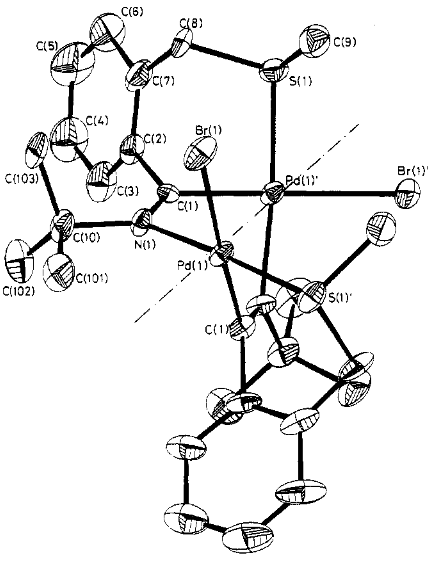
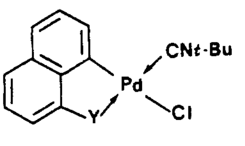


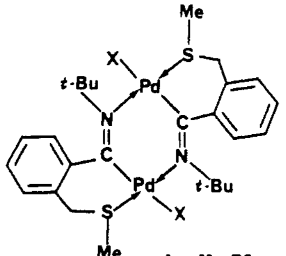
Figure 1. ORTEP view of compound 4• with the atom labeling scheme. Ellipsoids represent 30% probability. Bond lengths (Å): Pd(1)–N(1), 2.096 (6); Pd(1)–C(1); 1.966 (7); Pd(1)–Br (1), 2.544 (1); Pd(1)–S(1); 2.293 (2); C(1)–N(1) 1.273 (9); Pd(1)–Pd(1), 2.894 (1). Bond angles (deg): S(1)′ – Pd(1)–Br(1), 89.75 (6)′,C(1)′–Pd(1)–Br(1), 175.9 (2); C(1)′–Pd(1)–S(1), 90.3 (2); N(1)–Pd(1)–S(1)′, 175.2 (2); N(1)–Pd(1)–Br(1), 95.0 (2); N(1)–Pd(1)–C(1)′, 85.0 (3).

Treating suspensions of **2a** or **2b**, in dichloromethane at room temperature, with 2 molar equiv of *t*-BuNC immediately afforded pale yellow solutions, from which the monomeric complexes **3a** and **3b** could be obtained quantitatively.[7–9] On the other hand, the corresponding monomeric compound derived from the reaction of **1a** with *t*-BuNC was not isolated as the solution turned rapidly orange, affording complex **4** as red crystals in quantitative yield. The spectroscopic and analytical data[7–9] of the latter compound suggest the dimeric structure depicted, which has been confirmed for the bromine derivative 4•[10] by an X-ray diffraction study.[11] The structure is shown in Figure 1 together with relevant bond distances and angles. It is at once apparent that the *t*-BuNC has inserted into the Pd–C bond of **1a** giving rise to a six-membered cyclopalladated ring with a chair conformation. The molecule has a crystallographic twofold axis which relates two asymmetric units [$C_{13}H_{18}BrNSPd$] through two C═N



3a, Y= SMe

3b, Y= NMe_2



4 , X=Cl

4•, X=Br

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(4) Compound **2a** was obtained by reaction of methyl 1-naphthyl sulfide with palladium acetate in acetic acid at reflux temperature followed by methathesis of the acetato bridges with lithium chloride in acetone.

(5) The previous palladated thioether ligands differed from ours by the fact that the sulfur atoms were substituted by bulky groups.[6]

(6) Fushita, Y.; Hiraki, K.; Yamaguchi, T.; Maruta, T. *J. Chem. Soc., Dalton Trans.* **1981**, 2405. Rüger, R.; Rittner, W.; Jones, P. G.; Isenberg, W.; Sheldrick, G. M. *Angew. Chem.* **1981**, *93*, 389. Errington, J.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 2312.

(7) Anal. Calcd for $C_{22}H_{18}S_2Cl_2Pd_2$ (**2a**): C, 41.94; H, 2.88. Found: C, 41.89; H, 2.57. Anal. Calcd for $C_{16}H_{18}NSClPd$ (**3a**): C, 48.25; H, 4.56; N, 3.52. Found: C, 48.24; H, 4.46; N, 3.62. Anal. Calcd for $C_{17}H_{21}N_2ClPd$ (**3b**): C, 51.66; H, 5.34; N, 7.04. Found: C, 51.30; H, 5.32; N, 6.82. Anal. Calcd for $C_{26}H_{36}N_2S_2Cl_2Pd_2$ (**4**): C, 43.10; H, 5.01; N, 3.87. Found: C, 42.98; H, 4.89; N, 3.64. Anal. Calcd for $C_{26}H_{36}N_2S_2Br_2Pd_2$ (**4•**): C, 38.39; H, 4.46; N, 3.44. Found: C, 37.90; H, 4.36; N, 3.27. Anal. Calcd for $C_{21}H_{27}N_2SClPd$ (**5**): C, 52.39; H, 5.65; N, 5.82. Found: C, 52.10; H, 5.71; N, 5.72. Anal. Calcd for $C_{18}H_{18}S_2O_2Cl_2Pd_2$ (**6**): C, 35.20; H, 2.95. Found: C, 35.03; H, 3.01. Anal. Calcd for $C_{24}H_{18}S_2O_2Cl_2Pd_2$ (**8**): C, 42.00; H, 2.64. Found: C, 41.66; H, 2.59.

(8) Infrared (cm^{-1}, KBr pellets): **3a**, 2200 (ν (C≡N)); **3b**, 2198 (ν (C≡N)); **4**, 1670 (ν (C═N)); **4•**, 1665 (ν (C═N)); **5**, 2195 (ν (C≡N)), 1645 (ν (C═N)); **7**, 1660 (ν (C═O)); **8**, 1670 (ν (C═O); **9**, 2050 (ν (C≡O)).

(9) ^1H NMR (200 MHz, $CDCl_3$, 20 °C): **2a**, δ 2.75 and 3.00 (2s, 6 H, SMe), cis and trans isomers; **3a**, δ 3.35 (s, 3 H, SMe), 1.63 (s, 9 H, *t*-Bu); **3b**, 3.35 (s, 6 H, NMe_2), 1.63 (s, 9 H, *t*-Bu); **4**, δ 3.06 and 3.36 (2d, 2 H, CH_2S, $^2J_{H-H}$ = 11.8 Hz), 3.01 (s, 3 H, SMe), 1.43 (s, 9H, *t*-Bu); **4•**, δ 3.12 and 3.42 (2d, 2 H, CH_2S, $^2J_{H-H}$ = 11.3 Hz), 3.08 (s, 3 H, SMe), 1.41 (s, 9 H, *t*-Bu); **5**, 2.89 (s, 3 H, SMe), 1.71 and 1.42 (2s, 18 H, *t*-Bu).

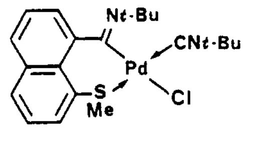
(10) This compound was obtained by treating **4** with excess of LiBr in acetone. Crystals suitable for X-ray analysis were obtained from a dichloromethane/hexane solution.

(11) Crystal structure of **4•**: $[C_{13}H_{18}BrNSPd]_2$, M_r 813.3, tetragonal, space group $I4_1/a$, a = 17.443 (2) Å, c = 22.412 (9) Å, U = 6821; ρ_{calcd} (Z = 8) = 1.58 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 36.5 cm^{-1}. A crystal of 0.32 × 0.27 × 0.24 mm was used. Of a total of 3858 reflections, collected on a Enraf-Nonius CAD-4 diffractometer in the range $3 < 2\theta < 50°$, 1669 reflections with $I > 3\sigma(I)$ were observed. No absorption correction was applied. The structure was solved by the Patterson heavy-atom method which revealed the Pd and Br atoms. All other atoms were located on subsequent electron density and difference electron density maps. The structure was refined by full-matrix least-squares techniques (with all non-hydrogen atoms assigned anisotropic temperature factors) to R = 0.0417 and R_w = 0.0460, using the CRYSTALS program library.[12]

(12) Carruthers, B.; Watkin, D. J. CRYSTALS, an Advanced Crystallographic Computer Program; Chemical Crystallography Laboratory: University of Oxford, Oxford, England, 1985.

bridges. The nitrogen atom of the inserted isocyanide is strongly bonded to the second palladium atom, leading to a short Pd–Pd contact (2.894 (1) Å), which is comparable to those found in related compounds in which the two palladium atoms are bridged by acetato groups[13] or orthopalladated pyridines.[14] Analogous dimetallic compounds obtained via insertion of isocyanide into the Pd–C bond have been reported recently, but no structural characterization have so far been performed.[15] This very rapid insertion of a *t*-BuNC into the Pd–C bond of **1a** is markedly different from the behavior observed for complex **1b**,[16] which, under the conditions used here (i.e., using the same stoichiometry), was resistant to the insertion of *t*-BuNC into its Pd–C bond. Similarly, in presence of an excess of this reagent, complex **2a** is rapidly transformed into compound **5**, in which one isocyanide has been inserted into the Pd–C bond, whereas, for complex **2b**, no insertion has taken place even when the reaction was conducted in refluxing chlorobenzene.

The reaction of compound **1b** with carbon monoxide has been investigated in detail.[3a] Usually it affords mixtures of organic products through the reductive elimination of palladium metal, the nature of the carbonylation products depending on various factors such as, for example, the solvent, the anionic ligand on the palladium, etc. We found that **1b** in dichloromethane under CO (2 atm) gave only the heterocycle **6** in quantitative yield. When a suspension of **1a** in dichloromethane was treated with carbon monoxide (2 atm) a pale yellow solution resulted from which, after a few minutes, compound **7** precipitated as an insoluble solid. The infrared of the latter shows a strong absorption at 1660 cm^{-1}; the ^{1}H NMR data[17] indicate the presence of a six-membered ring, which is fluxional in solution, a feature that has been described recently for other metallocyclic units of this type.[18] These results strongly suggest that the insertion of carbon monoxide into the Pd–C bond of **1a** has indeed taken place.



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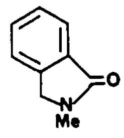

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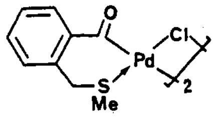
The influence of the donor atom on the ease of insertions of CO is also obvious when comparing the reactions of complexes **2a** and **2b** with this reagent. As found for **1a**, complex **2a** reacted with CO to give the insertion product **8**,[17] whereas complex **2b**, under the same conditions, afforded complex **9** in which the CO is terminally bonded to the palladium center.



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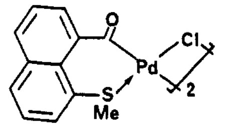

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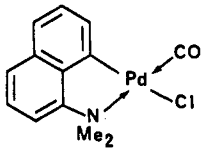

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An interesting feature of the reaction of CO with compounds **1a** and **2a** is its reversibility that was observed under very mild conditions. When **7** or **8** was heated at 35 °C in dichloromethane, the cyclopalladated compounds **1a** and **2a**, respectively, were quantitatively regenerated. This "insertion–deinsertion" of CO into the Pd–C bonds could be repeated several times without any decomposition products being observed.

These results have clearly demonstrated that the replacement of the NMe$_2$ unit by SMe in the palladocycles increases the ease of insertion of nucleophiles, such as *t*-BuNC or carbon monoxide into the Pd–C bond. This chemical behavior is in marked contrast to our recent results[3h,19] which indicated that the insertion of substituted alkynes into the Pd–C bonds of the cyclopalladated compounds occurs more easily with the nitrogen-containing cyclopalladated compounds.

Acknowledgment. We thank the CNPq (Brazil) for a fellowship (to J.D.).

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances and angles, and selected least-squares best planes (4 pages); listings of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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(13) See for instance: Churchill, M. R.; Wasserman, H. J.; Glenda, J. Y. *Inorg. Chem.* **1980**, *19*, 762. Selbin, J.; Abbоud, K.; Watkins, S. F.; Gutierrez, M. A.; Fronczek, F. R. *J. Organomet. Chem.* **1983**, *241*, 259.

(14) Isobe, K.; Nanjo, K.; Nakamura, Y.; Kawaguchi, S. *Bul. Chem. Soc. Jpn.* **1986**, *59*, 2141.

(15) Uson, R.; Fornies, J.; Espinet, P.; Pueyo, L. *J. Organomet. Chem.* **1986**, *299*, 251.

(16) Yamamoto, Y.; Yamazaki, H. *Inorg. Chim. Acta* **1980**, *41*, 229.

(17) Due to the poor solubility of this compound in all solvents its ^{1}H NMR spectrum was obtained in the presence of pyridine-d_5 so that we ran in fact the spectrum of the monomeric pyridine adduct of the dimer **7** (CD_2Cl_2 + $\sum$py-d_5): at 20 °C, δ 3.47 (s, 2 H, CH_2SMe), 2.58 (s, 3 H, SMe); at −80 °C, δ 3.48 and 3.30 (2d, 2 H, CH_2SMe, $^2J_{H-H}$ = 13.8 Hz), 2.52 (s br, 3 H, SMe). **8** ($CDCl_3$ + $\sum$py-d_5): δ 2.63 (s br, 3 H, SMe).

(18) Hiraki, K.; Fuchita, Y.; Takechi, K. *Inorg. Chem.* **1981**, *20*, 4316.

(19) We found that compound **2a** resisted all attempts to insert any type of alkyne into its Pd–C bond.