orbital is identified as I_i. In Figure 15a, we illustrate the convolution for the $[Ni(MoS_4)_2]^{2-}$ complex ion. Ionization from orbitals that have large contribution from the Ni d bases are identified in the figure as $I_1(5b_{2g})$, $I_2(3b_{3g})$, and $I_5(4b_{2g})$. Peaks $I_3(4b_{1u})$ and $I_4(2a_u)$ are not identified because they involve orbitals that have no contribution from the central metal d bases. In the case of the Pd complex ion, there is only one ionization peak that involves orbitals with appreciable Pd(d) bases and it is identified as $I_3(3b_{3g})$. The relative composition of the d component is seen to be much smaller than in the nickel analogue. In $[Pt(MoS_4)_2]^{2-}$ we identify three ionization peaks, namely I_1, I_2, and I_5 that are equivalent to the $[Ni(MoS_4)_2]^{2-}$ analogue but have a smaller contribution from the central metal d component. It is also apparent that the contribution of the d component in the higher occupied orbitals is much larger in the $[Ni(MoS_4)_2]^{2-}$ complex ion. The reverse is true for the lower occupied orbitals. It is only unfortunate that there is no experimental data regarding the ionization energies of these species that one can compare with and these values are included only for future validation. We point out, however, that Xα binding energies are reported to be overestimated by ~20%. Binding energies of carbonyl to a single Pd atom or to a Pd dimer have been reported by Blomberg et al.[55] by employing a large basis set using the size-consistent coupled pair functional with CI. The chemisorption energy of CO on a Pd surface is determined by these authors to be much smaller than the binding energy to the dimer and is therefore consistent with relativistic Xα calculations using the LCGTO-VWN model potential on the same system reported by Andzelm and Salahub.[56]

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Registry No. $[NiMo_2S_8]^{2-}$, 66616-04-4; $[PdMo_2S_8]^{2-}$, 71035-56-8; $[PtMo_2S_8]^{2-}$, 71035-58-0; $[NiW_2S_8]^{2-}$, 45845-07-6; $[PdW_2S_8]^{2-}$, 71035-57-9; $[PtW_2S_8]^{2-}$, 71035-59-1.

Supplementary Material Available: Tables IV-VIII listing molecular orbital energies and charge compositions of the MO's (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Departamento de Química Inorgânica, Universidad de Murcia, 30071-Murcia, Spain,
Departamento de Química, Universidad Autônoma de Barcelona, 08193-Bellaterra, Barcelona, Spain,
and Instituto de Ciencia de Materiales CSIC, Martí y Franquês s/n, 08028 Barcelona, Spain

Synthesis, Structural Characterization, and Reactivity toward Weak, Protic Electrophiles of $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$

Gregorio López,*[†] José Ruiz,[†] Gabriel García,[†] Consuelo Vicente,[†] Jaime Casabó,[‡] Elies Molins,[§] and Carlos Miravitlles[§]

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The bis(μ-hydroxo) complex $Q_2[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ (**1**) (Q = NBu_4) has been obtained by reaction of *cis*-$Pd(C_6F_5)_2(PhCN)_2$ with 20% aqueous QOH in acetone. **1** reacts with weak, protic electrophiles H(LL) in the 1:2 molar ratio to give $Q_2[(C_6F_5)_2Pd(\mu\text{-}LL)_2Pd(C_6F_5)_2]$ [LL = pyrazolate (**2**), 3,5-dimethylpyrazolate (**3**), 3-methylpyrazolate (**4**), indazolate (**5**)]. The reaction between **1** and H(LL) (acetylacetone, benzoylacetone, 8-hydroxoquinoline) in acetone leads to the formation of the corresponding mononuclear complexes $Q[(C_6F_5)_2Pd(LL)]$ (**6**-**8**). $Q_2[(C_6F_5)_2Pd(\mu\text{-}OH)(\mu\text{-}dmpz)Pd(C_6F_5)_2]$ (**9**) has been produced by treatment of $Q_2[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(C_6F_5)_2]$ with QOH and Hdmpz (1:2:1 molar ratio) in methanol. IR and ^1H and ^{19}F NMR spectra have been used for structural assignments. An X-ray structural determination, carried out with $(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$, has established the centrosymmetric binuclear nature of the anion, and the geometry around each Pd atom is that of a distorted planar square with Pd-O = 2.077 (6) and 2.068 (6) Å and Pd-C distances of 1.997 (7) and 2.006 (6) Å.

Introduction

The relative paucity of hydroxo complexes of the late transition metals has been attributed to the commonly believed reason that the M-OH bonds should be intrinsically weak owing to the mismatch of a hard, basic ligand (OH^-) with a soft metal center. The relatively recent work, however, suggests that the L_nM-OH bonds in hydroxo complexes are stronger than L_nM-C bonds in alkyl complexes.[1]

Synthetic routes used to prepare monomeric hydroxo complexes[1] of the nickel group elements include metal exchange,[2-4] oxidative addition,[5] and irreversible,[6] or reversible,[2a,b,3b,6d,7,8] σ-ligand metathesis reactions. Recently, some hydroxo-bridged complexes of nickel,[9a,b] palladium,[10] and platinum[10-12] have been described.

The recent surge of interest in the chemistry of hydroxo complexes of the nickel group elements is undoubtedly related to their interesting reactivity and potential relevance to catalysis.

On the other hand, in the reported $K_2[Pd(C_6F_5)_4]$-catalyzed cyclotrimerization of malononitrile,[13] the identity of the actual catalyst was left unexplored. The presence of a hydroxo-palladium species, generated in situ by hydrolysis of $[Pd(C_6F_5)_4]^{2-}$, could

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[†] Universidad de Murcia.
[‡] Universidad Autônoma de Barcelona.
[§] Instituto de Ciencia de Materiales.

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Table I. NMR Data (ppm) for the Palladium Complexes

complex	^1H ($SiMe_4$)[a]	^{19}F ($CFCl_3$)
1[b]	−2.84 (s, 2 H, OH)	−115.6 (d, 8 F_o, $J_{o,m}$ = 27.3 Hz) −164.9 (t, 4 F_p, $J_{m,p}$ = 20.1 Hz) −166.4 (m, 8 F_m)
2[c]	7.05 (d, 4 H, 3- and 5-H, J = 1.9 Hz) 5.70 (t, 2 H, 4-H, J = 1.9 Hz)	−110.7 (d, 8 F_o, $J_{o,m}$ = 25.6 Hz) −165.7 (m, 4 F_p + 8 F_m)
3[c]	5.16 (s, 2 H, 4-H) 1.81 (s, 12 H, CH_3)	−107 (br, 8 F_o) −168 (m, 4 F_p + 8 F_m)
4[c]	7.39 (d, 2 H, 5-H, J = 1.6 Hz) 5.47 (d, 2 H, 4-H, J = 1.6 Hz) 1.84 (s, 6 H, CH_3)	−108.5 (br, 2 F_o) −109.9 (br, 2 F_o) −113.1 (br, 2 F_o) −115.2 (br, 2 F_o) −164.5 (m, 4 F_p + 8 F_m)
5[c]	8.15 (s, 2 H) 7.44 (d, 2 H, J = 8.4 Hz) 7.37 (d, 2 H, J = 8.1 Hz) 6.77 (pseudotriplet, 2 H, J = 7.4 Hz) 6.59 (pseudotriplet, 2 H, J = 7.2 Hz)	−109.5 (br, 4 F_o) −112.7 (br, 4 F_o) −166.6 (m, 4 F_p + 8 F_m)
6[b]	5.24 (s, 1 H, CH) 1.82 (s, 6 H, CH_3)	−115.9 (d, 4 F_o, $J_{o,m}$ = 26.0 Hz) −164.2 (t, 2 F_p, $J_{m,p}$ = 20.0 Hz) −166.0 (m, 4 F_m)
7[b]	7.64 (d, 2 H, aromatic, J = 6.9 Hz) 7.21 (m, 3 H, aromatic) 5.87 (s, 1 H, CH) 1.92 (s, 3 H, CH_3)	−116.3 (br, 4 F_o) −164.03 (t, 1 F_p, $J_{m,p}$ = 19.3 Hz) −164.07 (t, 1 F_p, $J_{m,p}$ = 18.0 Hz) −165.9 (m, 4 F_m)
8[b]	8.08 (d, 1 H, J = 7.9 Hz) 7.64 (d, 1 H, J = 4.7 Hz) 7.30 (pseudotriplet, 1 H, J = 7.9 Hz) 7.11 (dd, 1 H, J 7.9 Hz, J' = 4.7 Hz) 6.83 (pseudotriplet, 2 H, J = 7.9 Hz)	−114.0 (d, 2 F_o, $J_{o,m}$ = 32.6 Hz) −115.0 (d, 2 F_o, $J_{o,m}$ = 30.0 Hz) −163.0 (t, 1 F_p, $J_{m,p}$ = 19.6 Hz) −163.9 (t, 1 F_p, $J_{m,p}$ = 19.9 Hz) −165.2 (m, 4 F_m)
9[b]	5.39 (s, 1 H, 4-H) 1.54 (s, 6 H, CH_3) −1.53 (s, 1 H, OH)	−113.6 (d, 4 F_o, $J_{o,m}$ = 29.6 Hz) −114.6 (d, 4 F_o, $J_{o,m}$ = 28.5 Hz) −164.5 (t, 2 F_p, $J_{m,p}$ = 20.4 Hz) −166.3 (m, 2 F_p + 8 F_m)

[a] Additional peaks (ppm) of $(NBu_4)^+$ are found at ca. 3.7 (t, N-CH_2), 1.8 (m, N–CH_2–*CH_2*), 1.5 (m, *CH_2*–CH_3), and 1.0 (t, CH_3), the relative intensities being 16:16:16:24 (**1–5**, **9**) or 8:8:8:12 (**6–8**). [b] In $CDCl_3$. [c] In $(CD_3)_2CO$.

account for the catalytic process. Further investigation has revealed that $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$ can be conveniently prepared under appropriate conditions. Here we report on the synthesis, characterization, and chemical reactivity toward some weak acids of the above hydroxo–organopalladium complex.

Partial data for $[(C_6F_5)_2M(\mu\text{-}OH)_2M(C_6F_5)_2]^{2-}$ (M = Ni, Pd, Pt) have been briefly communicated.[14]

Results

Table II. Crystallographic Data for Complex **1**

$C_{24}H_2O_2F_{20}Pd_2\cdot 2C_{16}H_{36}N$	fw 1400.1
a = 12.564 (7) Å	space group $P2_1/c$ monoclinic
b = 12.985 (12) Å	λ = 0.71069 Å (Mo Kα)
c = 19.290 (14) Å	ρ_{calcd} = 1.53 g cm^{-3}
β = 104.51 (3)°	μ = 6.8 cm^{-1}
V = 3047 (4) Å^3	R = 0.051
Z = 2	R_w = 0.059
T = 21 °C	

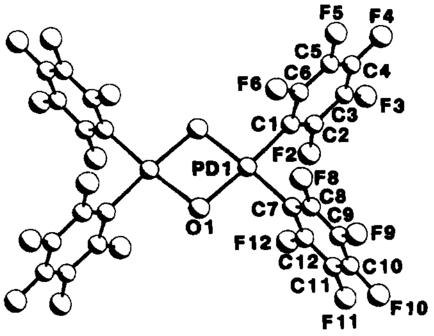

Figure 1. Molecular structure and atom-labeling scheme for $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$.

Synthesis and Characterization of $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$. In acetone solution, *cis*-$Pd(C_6F_5)_2(PhCN)_2$ reacts readily with 20% aqueous QOH (Q = NBu_4) to give the bis(μ-hydroxo) complex **1** (eq 1). The IR spectrum of **1** shows the

$$2\,cis\text{-}Pd(C_6F_5)_2(PhCN)_2 + 2QOH \rightarrow Q_2[\{(C_6F_5)_2Pd\}_2(\mu\text{-}OH)_2] + 4PhCN \quad (1)$$

absorptions attributed to the C_6F_5 group[15] at 1630 m, 1490 vs, 1450 vs, 1050 vs, and 950 cm^{-1} vs and a split band at ca. 800 cm^{-1} (X-sensitive mode of C_6F_5[16]), which is characteristic of the *cis*-$Pd(C_6F_5)_2$ fragment.[17,18] The IR spectrum also gives evidence of the hydroxo group: 3610 m (OH stretch[19]) and 460 cm^{-1} s (Pd–O stretch[20]) although the OH bending mode, usually observed[20] in the region 1100–900 cm^{-1}, should be obscured by the strong absorption of the C_6F_5 group at 1050 cm^{-1}. Further evidence for the presence of the OH groups comes from the ^1H NMR spectrum, which displays a resonance at δ −2.84, in

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Table III. Fractional Atomic Coordinates ($\times 10^4$) with Their Equivalent Isotropic Temperature Factors (Å^2)

	x/a	*y/b*	*z/c*	B_{eq}
Pd1	3866.4 (0.5)	471.8 (0.5)	10046.6 (0.4)	6.36
O1	4999 (6)	602 (7)	9430 (5)	14.39
F2	1575 (4)	−679 (4)	9798 (3)	8.23
F3	230 (4)	−963 (5)	10648 (3)	9.33
F4	704 (4)	−133 (5)	11987 (3)	8.46
F5	2612 (5)	919 (5)	12473 (3)	8.70
F6	4009 (4)	1161 (4)	11644 (3)	7.94
F8	3495 (4)	2803 (4)	10398 (3)	7.52
F9	2287 (5)	4283 (4)	9657 (3)	9.09
F10	940 (4)	3886 (5)	8350 (3)	9.88
F11	853 (5)	1976 (6)	7812 (3)	11.45
F12	2098 (5)	459 (4)	8531 (3)	9.53
N1	7175 (4)	2791 (4)	11533 (3)	4.75
C1	2849 (5)	268 (5)	10681 (4)	4.61
C2	1886 (6)	−264 (5)	10458 (4)	4.97
C3	1167 (6)	−407 (6)	10898 (5)	5.78
C4	1409 (7)	−1 (7)	11563 (5)	5.55
C5	2352 (6)	538 (6)	11802 (4)	5.44
C6	3050 (6)	640 (6)	11364 (5)	5.18
C7	2848 (5)	1547 (5)	9500 (4)	4.11
C8	2840 (5)	2538 (6)	9751 (4)	4.38
C9	2248 (6)	3313 (6)	9380 (5)	5.30
C10	1581 (7)	3138 (8)	8732 (6)	6.27
C11	1535 (7)	2162 (10)	8465 (5)	7.00
C12	2178 (6)	1402 (6)	8843 (5)	5.26
C13	6522 (6)	3549 (5)	11878 (4)	4.99
C14	5466 (6)	3128 (6)	11983 (4)	5.96
C15	4930 (7)	3887 (7)	12412 (5)	7.24
C16	3868 (8)	3550 (8)	12501 (5)	8.74
C17	7435 (6)	1827 (6)	11971 (4)	5.84
C18	8010 (7)	1964 (7)	12764 (5)	7.11
C19	8126 (9)	1011 (8)	13173 (5)	8.89
C20	8612 (9)	1142 (9)	13958 (5)	8.98
C21	8255 (6)	3353 (5)	11514 (4)	5.09
C22	9010 (6)	2775 (6)	11177 (4)	5.99
C23	9970 (7)	3489 (6)	11097 (5)	6.43
C24	10810 (8)	2927 (8)	10837 (5)	8.57
C25	6534 (6)	2492 (6)	10785 (4)	5.50
C26	6223 (7)	3374 (7)	10274 (4)	6.87
C27	5737 (9)	3026 (9)	9513 (5)	8.86
C28	5266 (10)	3888 (10)	9020 (7)	11.25

agreement with the data reported for compounds containing Pd–OH bonds.[7] The ^{19}F spectrum exhibits the expected three signals for the *o*-, *m*-, and *p*-fluorine atoms in the C_6F_5 rings (Table I).

The structure of $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$ has been determined by single-crystal X-ray diffraction. Crystal data and data collection and refinement parameters are summarized in Table II. Positional and equivalent isotropic temperature factors are listed in Table III, and selected bond distances and angles are given in Table IV. Figure 1 shows the structure of the complex anion, which sits on a crystallographic center, so the core group Pd_2O_2 is strictly planar. The Pd–O distances are 2.068 (6) and 2.077 (6) Å, and the OPdO and PdOPd angles, 81.2 (4) and 98.8 (4)°, respectively. The bond angles in the Pd_2O_2 ring agree with the corresponding values found in bis(μ-hydroxo)platinum dimers[21] (PtOPt and OPtO angles of 100 and 80°, respectively), but in $[(o\text{-}Me\text{-}C_6H_4CH_2)(PMe_3)Ni(\mu\text{-}OH)]_2$ these structural parameters[9b] are appreciably smaller (NiONi = 91.0°, ONiO = 78.2°), as expected. The Pd···Pd distance is 3.147 (1) Å, showing no significant metal–metal interaction. The two C_6F_5 groups attached to the same Pd atom are perpendicular each other, and the angle between mean planes is 90.1°. Angles between mean planes defined by C_6F_5 groups and the Pd–O core are 75.5 and 78.1°, respectively.

Table IV. Bond Distances (Å) and Bond Angles (deg)[a]

O1–Pd1	2.077 (6)	C12–C7	1.347 (10)
O1*–Pd1	2.068 (6)	C9–C8	1.346 (9)
C1–Pd1	1.997 (7)	C10–C9	1.340 (12)
C7–Pd1	2.006 (6)	C11–C10	1.363 (13)
C2–F2	1.347 (8)	C12–C11	1.365 (12)
C3–F3	1.362 (8)	C13–N1	1.535 (8)
C4–F4	1.358 (8)	C17–N1	1.500 (9)
C5–F5	1.347 (9)	C21–N1	1.549 (8)
C6–F6	1.370 (8)	C25–N1	1.516 (9)
C8–F8	1.355 (8)	C14–C13	1.496 (10)
C9–F9	1.364 (9)	C15–C14	1.545 (11)
C10–F10	1.355 (9)	C16–C15	1.456 (12)
C11–F11	1.356 (9)	C18–C17	1.530 (11)
C12–F12	1.357 (8)	C19–C18	1.456 (12)
C2–C1	1.366 (9)	C20–C19	1.492 (13)
C6–C1	1.366 (11)	C22–C21	1.482 (09)
C3–C2	1.398 (10)	C23–C22	1.559 (10)
C4–C3	1.349 (11)	C24–C23	1.472 (11)
C5–C4	1.354 (11)	C26–C25	1.498 (10)
C6–C5	1.367 (10)	C27–C26	1.510 (13)
C8–C7	1.376 (9)	C28–C27	1.492 (14)
C1–Pd1–O1	175.8 (0.2)	C5–C6–F6	116.2 (0.7)
C7–Pd1–O1	94.6 (0.2)	C5–C6–C1	124.7 (0.7)
C7–Pd1–C1	89.6 (0.2)	C8–C7–Pd1	121.7 (0.6)
Pd1–O1–Pd1*	98.8 (0.4)	C12–C7–Pd1	124.3 (0.5)
O1–Pd1–O1*	81.2 (0.3)	C12–C7–C8	113.9 (0.6)
C2–C1–Pd1	121.8 (0.6)	C7–C8–F8	120.4 (0.6)
C6–C1–Pd1	123.6 (0.5)	C9–C8–F8	115.2 (0.7)
C6–C1–C2	114.7 (0.6)	C9–C8–C7	124.3 (0.7)
C1–C2–F2	121.6 (0.6)	C8–C9–F9	121.5 (0.8)
C3–C2–F2	116.2 (0.6)	C10–C9–F9	118.3 (0.7)
C3–C2–C1	122.1 (0.7)	C10–C9–C8	120.2 (0.7)
C2–C3–F3	119.2 (0.8)	C9–C10–F10	122.2 (0.9)
C4–C3–F3	120.8 (0.7)	C11–C10–F10	119.9 (1.0)
C4–C3–C2	120.0 (0.7)	C11–C10–C9	117.8 (0.8)
C3–C4–F4	119.8 (0.8)	C10–C11–F11	118.2 (1.0)
C5–C4–F4	120.5 (0.8)	C12–C11–F11	121.2 (1.0)
C5–C4–C3	119.7 (0.7)	C12–C11–C10	120.5 (0.8)
C4–C5–F5	119.9 (0.7)	C7–C12–F12	120.2 (0.8)
C6–C5–F5	121.2 (0.8)	C11–C12–F12	116.6 (0.9)
C6–C5–C4	118.8 (0.8)	C11–C12–C7	123.2 (0.8)
C1–C6–F6	119.1 (0.7)		

[a] An asterisk indicates an atom with symmetry coordinates $1 - x$, $-y$, $2 - z$.

The angles of the ipso-carbons in C_6F_5 groups are 114.7 (6) and 113.9 (6)°, well below the ideal 120° value. Also, the C–C distances are significantly less than 1.395 Å. This decrease in bond lengths and angles in the perfluorophenyl rings has been pointed out by Jones[22] and confirms that C_6F_5 groups should not be refined as rigid bodies as has been usually done.

Reactivity of 1 toward Weak, Protic Electrophiles. The considerable nucleophilicity of the OH bridges in **1**, indicated by the high-field proton resonance, is consistent with the chemical reactivity exhibited by **1** toward H(LL) [1:2 molar ratio; H(LL) = pyrazole (Hpz), 3,5-dimethylpyrazole (Hdmpz), 3-methylpyrazole (Hmpz), indazole (Hind)] to give the complexes listed in Scheme I (**2**–**5**).

The IR spectra of **2**–**5** show the split band of the *cis*-$Pd(C_6F_5)_2$ moiety at ca. 800 cm^{-1}, and measurements of the molar conductivity in acetone solution are in accordance with the proposed formulas. ^1H and ^{19}F data for **2**–**5** are collected in Table I.

The ^1H NMR data of **2**–**5** are in agreement with the results reported for other μ-pyrazolate complexes,[23] and the ^{19}F spectra of **2** and **3** indicate the equivalence of the four C_6F_5 groups. Two broad resonances, in a 1:1 ratio, are observed for the *o*-fluorine atoms in the C_6F_5 rings in the ^{19}F spectra of **5**, as it is expected for the presence of asymmetric pyrazolate bridges (4 F_o trans to N^1:4 F_o trans to N^2). However, the ^{19}F NMR spectrum of **4** shows four *o*-fluorine resonances in a 1:1:1:1 ratio. In pyrazolate-bridged

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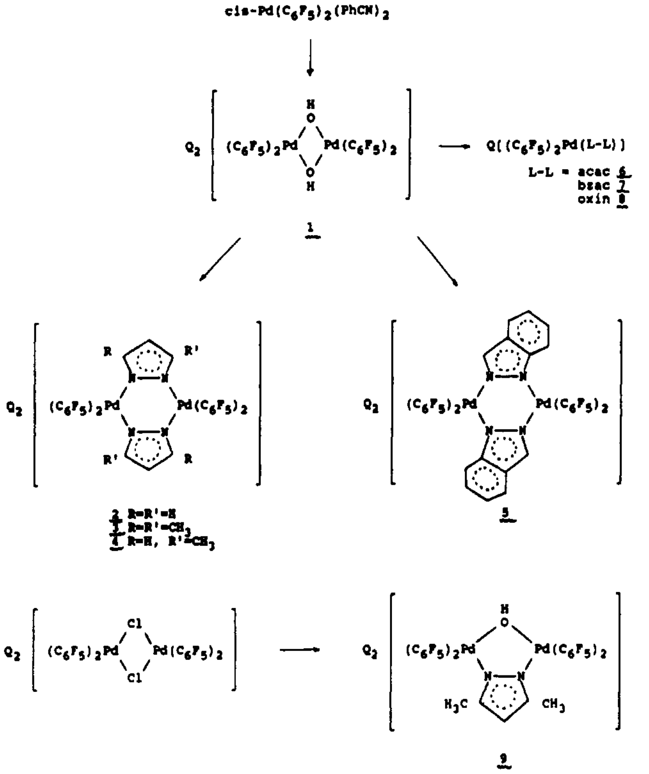
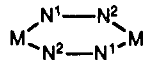
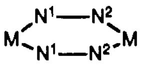
Scheme I. Synthesis and Reactivity of $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-}$ (Q = NBu_4)

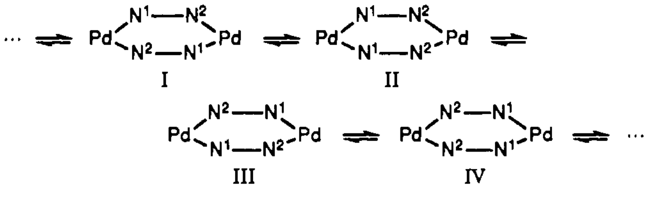


ruthenium(I) complexes, the presence of the possible isomers I and II (N^1–N^2 = mpz or ind) has been detected by ^{1}H NMR


I


II

spectroscopy[24] in chloroform solution, and two sets of resonances (I + II) are found in the spectra. In the ^{1}H spectra of **4** and **5**, however, only one set of sharp peaks is observed. The ^{1}H and ^{19}F NMR spectra of complex **4** were recorded at different temperatures. Although the ^{1}H NMR spectra remained unchanged between −70 and +50 °C, the ^{19}F NMR spectra showed significant changes in the *o*-fluorine region (see Figure 2), suggesting the existence of a dynamic chemical process involving structures I–IV.



At lower temperatures the interconversion rate is slower than the NMR time scale, so the ^{19}F spectrum exhibits the sharp signals (relative intensities 1:1:1:1) from structures I–IV, each one containing two pairs of equivalent C_6F_5 rings. Since I and III are equivalent, as are II and IV, one could expect four doublets by coupling to the *m*-fluorine atoms ($J_{o,m} \approx 33$ Hz). The triplet signals may be attributed to the C_6F_5 rings adjacent to the methyl groups (i.e., cis to N^2) on the assumption that the frequency separation of the *o*-fluorine resonances of these rings is equal in magnitud to $J_{o,m}$. The coalescence point could not be reached by increasing the temperature because the sample is not sufficiently soluble or decomposes in solvents other than acetone.

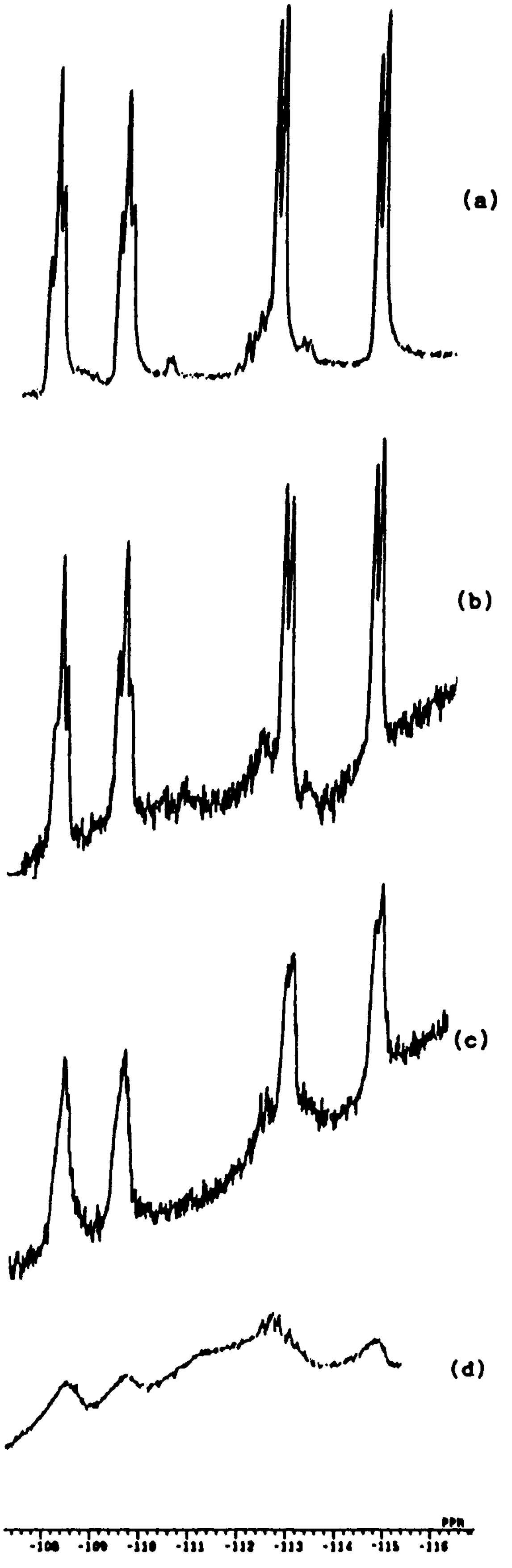


Figure 2. ^{19}F NMR spectra of complex **4** in the *o*-fluorine region only at 270 MHz in $(CD_3)_2CO$ at temperatures of −25 (a), 0 (b), +25 (c) and +50 °C (d). The spectra at −70 and −50 °C are identical with (a). The four resonances are observed at ca. −108.5, −109.9, −113.1, and −115.2 ppm (see text).

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1 also reacts with the weak acids acetylacetone (Hacac), benzoylacetone (Hbzac), and 8-hydroxyquinoline (Hoxin) to give compounds **6**–**8**. The IR spectra show again the split band at ca. 800 cm^{-1} attributed to the *cis*-$Pd(C_6F_5)_2$ fragment, and measurements of the molar conductivity in acetone indicate that **6**–**8** behave as 1:1 electrolytes. The ^1H and ^{19}F NMR data for these compounds are listed in Table I, and they are consistent with the presence of mononuclear anions containing $(LL)^-$ as a chelate ligand.

Discussion

The present study shows that *cis*-$[Pd(C_6F_5)_2(PhCN)_2]$ is a good precursor for the synthesis of the hydroxo complex **1** in high yield (85%), and the σ-ligand metathesis reactions between complex **1** and the weak acids H(LL) lead to the formation of bis(μ-pyrazolate) complexes. Intermediate aqua complexes formed by protonation of **1** by H(LL) as well as μ-hydroxo–μ-pyrazolate species should be involved in the formation of the bis(μ-pyrazolate) complexes (eq 2). In fact, such species have been detected or

$$[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]^{2-} \xrightarrow[-H_2O]{+H(LL)} [(C_6F_5)_2Pd(\mu\text{-}OH)(\mu\text{-}LL)Pd(C_6F_5)_2]^{2-} \xrightarrow[-H_2O]{+H(LL)} [(C_6F_5)_2Pd(\mu\text{-}LL)_2Pd(C_6F_5)_2]^{2-} \quad (2)$$

isolated for the rhodium–hydroxo–pyrazolate systems.[23a] In our study, Pd(μ-OH)(μ-LL)Pd species have been detected by ^1H NMR spectroscopy when **1** reacts with H(LL) (1:1 molar ratio) in acetone. The ^1H spectra of the isolated solids show the presence of **2**–**5** and the respective mono(hydroxo)–mono(pyrazolate) complexes, $[(C_6F_5)_2Pd(\mu\text{-}OH)(\mu\text{-}LL)Pd(C_6F_5)_2]^{2-}$ [LL = pz, δ 6.52 (d, 2 H, 3- and 5-H, *J* = 1.9 Hz), 5.70 (t, 1 H, 4-H, *J* = 1.9 Hz), −1.67 (s, 1 H, μ-OH); LL = dmpz, δ 5.39 (s, 1 H, 4-H), 1.54 (s, 6 H, CH_3), −1.53 (s, 1 H, μ-OH); LL = mpz, δ 6.54 (s, 1 H, 5-H), 5.52 (s, 1 H, 4-H), 1.46 (s, 3 H, CH_3), −1.60 (s, 1 H, μ-OH); LL = ind, δ 7.15 (s, 1 H), 6.63 (m, 2 H), 6.30 (m, 2 H), −1.53 (s, 1 H, μ-OH)]. Attempts to obtain pure μ-hydroxo–μ-pyrazolate complexes were unsuccessful because of the persistent problem of impurities of the corresponding bis(μ-pyrazolate) complexes. Nevertheless, the above assignment can be taken with absolute confidence, for the ^1H NMR data of the dmpz complex are in perfect concordance with those of a sample of $Q_2[(C_6F_5)_2Pd(\mu\text{-}OH)(\mu\text{-}dmpz)Pd(C_6F_5)_2]$ (Table I) prepared by a different strategy: in methanol, $[(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(C_6F_5)_2]^{2-}$ reacts with QOH and Hdmpz (1:2:1 molar ratio) to give **9** (eqs 3 and 4).

$$\text{Hdmpz} + 2\text{QOH} \rightarrow (\text{dmpz})^- + \text{OH}^- + 2\text{Q}^+ + H_2O \quad (3)$$

$$(\text{dmpz})^- + \text{OH}^- + [(C_6F_5)_2Pd(\mu\text{-}Cl)_2Pd(C_6F_5)_2]^{2-} \rightarrow [(C_6F_5)_2Pd(\mu\text{-}OH)(\mu\text{-}dmpz)Pd(C_6F_5)_2]^{2-} + 2Cl^- \quad (4)$$

It should be noted that the μ-OH resonance at −2.84 ppm in **1** moves to lower field (at ca. −1.6 ppm) in the μ-hydroxo–μ-pyrazolate complexes, a result that can be attributed to the increased electron delocalization in the bridging system when one μ-OH group is substituted by the pyrazolate ligand. By comparison of **9** with **1** and **2**, the ^{19}F resonances located in the spectrum of **9** at δ −114.6 (F_o) and −164.5 (F_p) can be assigned to the C_6F_5 groups trans to μ-OH, and the resonances at δ −113.6 (F_o) and −166.3 (F_p), to the C_6F_5 groups trans to μ-pyrazolate, whereas the *m*-F atoms of both C_6F_5 rings are included in the resonance at δ −166.3.

Experimental Section

C, H, and N analyses were carried out with a Perkin-Elmer 240 C microanalyzer. Melting points were determined on a Riechert microscope. Conductivities were measured in acetone solution ($c \approx 5 \times 10^{-4}$ mol L^{-1}) with a Philips PW 9501/01 conductimeter. The spectroscopic instruments used were a Perkin-Elmer Model 1430 for IR spectra and a Bruker Model AC 200E (^1H) or Varian Model FT 80A (^{19}F) for NMR spectra. The variable-temperature spectra were recorded on a Jeol GSX-270 spectrometer. $SiMe_4$ and $CFCl_3$ were used as internal standards, respectively.

The precursors *cis*-$Pd(C_6F_5)_2(PhCN)_2$[25] and $(NBu_4)_2[\{Pd(C_6F_5)_2(\mu\text{-}Cl)\}_2]$[17] were prepared as described in the literature. Solvents were dried before use.

Crystal Structure Analysis. A single crystal of $(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ (0.15 × 0.21 × 0.27 mm) was mounted at the end of a glass fiber and centered in the Enraf-Nonius CAD4 diffractometer geometry. Cell parameters were determined by least-squares fitting of 25 high-angle reflections. During the data collection the standard reflections were measured each 1 h of crystal X-ray exposition giving a 1% variation. The scan method was ω–2θ with the range of *hkl* ($-7 \le h \le 7$, $0 \le k \le 9$, $0 \le l \le 28$) corresponding to $2\theta_{max} = 50°$. Lorentz and polarization effects were corrected but not for absorption (range of transmission factors 0.87–0.93). The structure was solved by direct methods (MULTAN 11/84). The first straightforward run gave the positions of the Pd atom and part of the perfluorophenyl rings. Subsequent weighted Fourier synthesis showed the remaining positions of the non-H atoms. Refinement was carried out by using full-matrix least-squares methods (SHELX-76) with isotropic thermal parameters for the cation and anisotropic parameters for the anion.

Hydrogen atoms were introduced in calculated positions and were refined with constraints (riding on their bonded atom) during the last stages of the refinement. The final *R* factor 0.051 (R_w = 0.059, where $w = 1/(\sigma^2(F) + 0.00524F^2)$ over 2790 observed reflections ($I > 2\sigma(I)$). The maximum and minimum heights in the final difference Fourier synthesis are 0.51 and −0.68 e $Å^{-3}$.

$(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ (1). A 20% solution of $(NBu_4)OH$ (0.2 mmol) was added to an acetone (10 mL) solution of *cis*-$Pd(C_6F_5)_2(PhCN)_2$ (0.2 mmol). After 30 min with stirring, the solution was concentrated under reduced pressure until the corresponding hydroxo complex began to precipitate. Addition of a small amount of water caused complete precipitation of white crystals, which were collected by filtration, washed with water, and air-dried. Yield: 85%.

Anal. Calcd for $C_{56}F_{20}H_{74}N_2O_2Pd_2$: C, 48.0; H, 5.3; N, 2.0. Found: C, 48.3; H, 5.4; N, 2.0. Mp: 180 °C dec. Λ_M: 182 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 790 sh, 780 s (X-sensitive mode of C_6F_5), 3610 (OH), 406 s (Pd–O str).

$(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}pz)_2Pd(C_6F_5)_2]$ (2). Pyrazole (Hpz; 0.158 mmol) was added to a solution of **1** (0.079 mmol) in methanol (2 mL) and the mixture was stirred for 30 min, whereupon white crystals of the title compound precipitated. The compound was isolated by filtration and air-dried. Yield: 80%.

Anal. Calcd for $C_{62}F_{20}H_{78}N_6Pd_2$: C, 49.6; H, 5.2; N, 5.2. Found: C, 50.1; H, 5.3; N, 5.4. Mp: 273 °C dec. Λ_M: 206 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 800, 790 s (X-sensitive).

$(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}dmpz)_2Pd(C_6F_5)_2]$ (3). 3,5-Dimethylpyrazole (Hdmpz; 0.14 mmol) was added to a methanol (3 mL) solution of **1** (0.07 mmol). After being stirred for 30 min, the solution was vacuum-evaporated to dryness. The residue was extracted with dichloromethane, and addition of hexane led to the precipitation of white crystals, which were filtered off, washed with ethanol, and air-dried. Yield: 80%.

Anal. Calcd for $C_{66}F_{20}H_{86}N_6Pd_2$: C, 50.9; H, 5.6; N, 5.4. Found: C, 50.6; H, 5.6, N, 4.4. Mp: 230 °C dec. Λ_M: 182 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 780 s, 770 s (X-sensitive).

$(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-}LL)_2Pd(C_6F_5)_2]$ [μ-LL = mpz (4), ind (5)]. White crystals of both complexes were prepared according to the procedure for **2**. Yield: 75%.

4. Anal. Calcd for $C_{64}F_{20}H_{82}N_6Pd_2$: C, 50.3; H, 5.4; N, 5.4. Found: C, 50.8; H, 5.6; N, 5.3. Mp: 254 °C dec. Λ_M: 189 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 780 s, 770 s, (X-sensitive).

5. Anal. Calcd for $C_{70}F_{20}H_{82}N_6Pd_2$: C, 52.5; H, 5.2; N, 5.3. Found: C, 52.1; H, 5.2; N, 5.0. Mp: 262 °C dec. Λ_M: 191 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 785 s, 775 s (X-sensitive).

$(NBu_4)[Pd(C_6F_5)_2(LL)]$ [LL = acac (6), bzac (7), oxin (8)]. A 0.15-mmol amount of H(LL) (acetylacetone, benzoylacetone, 8-hydroxyquinoline) was added to a solution of **1** (0.075 mmol) in acetone (10 mL). The solution was stirred for 30 min and then concentrated under reduced pressure. Addition of ethanol–water resulted in the precipitation of **6**–**8** as white (**6**) or yellow (**7**, **8**) solids, which were filtered off and air-dried. Yields: 65–70%.

6. Anal. Calcd for $C_{33}F_{10}H_{43}NO_2Pd$: C, 50.7; H, 5.5; N, 1.8. Found: C, 51.0; H, 5.6; N, 1.7. Mp: 221 °C dec. Λ_M: 109 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 795 s, 785 s (X-sensitive), 1580 s (ν(C–C) + ν(C–O)), 1510 s (ν(C–O) + ν(C–C)), 1400 s (CH_3 def), 445 s (ring/def).[19]

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7. Anal. Calcd for $C_{38}F_{10}H_{45}NO_2Pd$: C, 54.1; H, 5.4; N, 1.7. Found: C, 54.1; H, 5.7; N, 2.0. Mp: 270 °C dec. Λ_M: 92 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 795 s, 785 s (X-sensitive), 1590 vs (ν(C–C) + ν(C–O)), 1560 vs (ν(C–O) + ν(C–C)), 1400 s (CH_3 def), 460 m (ring def).[19]

8. Anal. Calcd for $C_{37}F_{10}H_{42}N_2OPd$: C, 53.0; H, 5.2; N, 3.4. Found: C, 52.8; H, 5.1; N, 3.6. Mp: 262 °C dec. Λ_M: 92 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 795 s, 780 s (X-sensitive), 1565 s, 820 s.

$(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-OH})(\mu\text{-dmpz})Pd(C_6F_5)_2]$ (9). A 20% aqueous solution of $(NBu_4)OH$ (0.139 mmol) was added to a methanol (7 cm^3) solution of 3,5-dimethylpyrazole (0.0695 mmol). After 10 min with constant stirring, $(NBu_4)_2[(C_6F_5)_2Pd(\mu\text{-Cl})_2Pd(C_6F_5)_2]$ (0.0695 mmol) was added and the solution was stirred at room temperature for 1 h. The solvent was then partially evaporated under vacuum, and water was added until precipitation of a white solid, which was separated by filtration and dried in air. Yield: 66%.

Anal. Calcd for $C_{61}F_{20}H_{82}N_{44}OPd_2$: C, 49.6; H, 5.5; N, 3.8. Found: C, 50.4; H, 5.8; N, 3.4. Mp: 216 °C dec. Λ_M: 179 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 785 sh, 780 s (X-sensitive), 3605 m (ν(OH)), 430 br (Pd–O).

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Supplementary Material Available: Listings of full crystal data, anisotropic thermal parameters, and fractional atomic coordinates for hydrogen atoms (3 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka 577, Japan,
and Institute for Molecular Science, Myodaizi, Okazaki 444, Japan

Synthesis, Characterization, and Molecular Structures of Binary and Ternary Copper(I) Complexes with 1,5-Cyclooctadiene (cod): $[Cu(cod)_2]ClO_4$ and $[Cu(cod)(2,2'\text{-bipyridine})]PF_6$

Megumu Munakata,*[†] Susumu Kitagawa,[†] Hisao Shimono,[†] and Hideki Masuda[‡]

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Binary and ternary copper(I) complexes with 1,5-cyclooctadiene (cod), $[Cu(cod)_2]ClO_4$ (**1**) and $[Cu(cod)(bpy)]PF_6$ (**2**) (bpy = 2,2'-bipyridine) have been prepared. The crystal structures have been determined by using single-crystal X-ray diffraction methods. Compound **1** crystallizes in the orthorhombic space group *Pnma*, with a = 17.434 (7) Å, b = 10.597 (4) Å, c = 8.718 (2) Å, Z = 4, and R = 0.073 for 913 reflections. Crystals of **2** are triclinic, space group $P\bar{1}$, with a = 9.774 (3) Å, b = 11.482 (2) Å, c = 8.959 (2) Å, α = 90.60 (2)°, β = 106.62 (2)°, γ = 83.09 (2)°, Z = 2, and R = 0.062 for 1542 reflections. The geometry about the Cu atom coordinated to the four olefinic moieties of the two cod molecules is quasi-tetrahedral in **1**. The Cu–C(olefin) distances of 2.27 Å (average) are significantly longer than those found for copper(I) olefin complexes, and the C=C bond distances of 1.33 Å (average) of the coordinated cod are almost the same that of free cod. On the basis of the C=C distance, the stretching frequencies of the C=C bonds and the ^{1}H NMR chemical shifts of the olefinic protons, the Cu–olefin bonds in **1** were concluded to be dominated by σ donation from the olefinic moiety to the copper. The geometry about the Cu atom coordinated to two nitrogen atoms of bpy and two olefinic moieties of the cod molecule is a very distorted tetrahedron in **2**. The Cu–C distances of 2.06 Å (average) of one olefinic moiety of the cod molecule are significantly shorter than those of the other olefinic moiety (2.44 Å (average)). In response to this, the C=C bond distance (1.36 (1) Å) of the former is longer than that (1.33 (1) Å) of the latter.

Introduction

Copper–olefin bonding is of both practical and theoretical interest in view of the catalytic activity of copper(I) toward olefin activation[1] and its role in biological systems.[2-4] Through the crystallographic study of mixed-ligand copper(I) complexes of ethylene,[2,4a] the important contribution of σ donation in copper(I)–olefin bonding has been inferred. In other words, the π back-donation is very weak.[2] This is supported by the fact that the upfield shifts of ^{1}H NMR signals of the ethylene protons of the copper(I) complexes with ethylene are small compared with those of Ni(0) and Pt(0) complexes with ethylene.[3] The copper(I) complexes with ethylene so far reported contain electron-donor nitrogen-based ligands. Such a ligand causes a trans influence,[5] which results in the enhancement of π back-donation from a dπ orbital of the metal to a π^* orbital of the olefin at the trans position.[3] It is of interest, therefore, to know the structure and the copper–olefin bonding of a Cu(I)–olefin complex without any strong electron-donor ligand, i.e. a Cu(I) complex having only olefin molecules.

No crystal structures of copper(I) complexes with only olefins have been reported so far, because the complexes are quite unstable under ambient conditions. The instability is increased by use of chelating dienes rather than monodentate olefins. A ternary copper(I) complex with 1,5-cyclooctadiene (cod) and chloride has been reported to have a centrosymmetric dimeric structure with the copper atoms quasi-tetrahedrally bonded to chlorine atoms and the two double bonds of the cod molecule.[6] Crystals of a copper(I) complex with two cod molecules, $[Cu(cod)_2]ClO_4$, have been prepared by electrolysis at a copper electrode of copper(II) perchlorate in the presence of cod in methanol.[7] The C=C stretching band at 1660 cm^{-1} in free cod is replaced by two bands at 1638 and 1595 cm^{-1} in the complex, suggesting nonequivalent coordination of the double bonds. We have synthesized suitable single crystals of the four-coordinate copper(I) complexes with

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[†] Kinki University.
[‡] Institute for Molecular Science.

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