Calcd for $C_{75}H_{66}O_2P_6Pt_2S$: C, 56.0; H, 4.1. Found: C, 55.9; H, 3.9%. MS: *m/e* 1607 (P), 1404 (P – P(O)Ph_2 = 1406), 1203 (P – 2{P(O)Ph_2 = 1205}). $^{31}P\{^1H\}$ NMR (in acetone-d_6): δ (ppm) = –13.3 [s, 2 P, $^1J(PtP)$ = 3510 Hz, $^2J(PtP)$ = –80 Hz, $^1J(PtPt)$ = 3100 Hz, P^a], 10.7 [m, 2 P, $^3J(P^bP^b)$ = 190 Hz, $^1J(PtP)$ = 3230 Hz, $^2J(PtP)$ = 200 Hz, P^b], 18.2 [m, 2 P, P^c].

Reaction of 1 with I_2. To a solution of **1** (50 mg, 0.03 mmol) in acetone (5 mL) was added iodine (15 mg, 0.06 mmol). The mixture was stirred for 0.5 h. The resultant yellow precipitate was collected, washed with pentane (10 mL), and dried in vacuo to yield [PtI_2(dppm)]. Yield: 13 mg, 0.01 mmol, 33%. $^{31}P\{^1H\}$ NMR (in $CDCl_3$): δ (ppm) = –68.0 [s, $^1J(PtP)$ = 3080 Hz].

[$Pt_4Me_4(\mu_4$-S)(μ-dppm)$_3$] (5a). To a solution of **1** (38 mg, 0.02 mmol) in acetone (5 mL) was added [$Pt_2Me_4(\mu$-$SMe_2)_2$] (14 mg, 0.02 mmol) in acetone (3 mL). The reaction mixture was stirred for 0.5 h. The solvent was removed in vacuo. The yellow residue was recrystallized from CH_2Cl_2/pentane. Yield: 30 mg, 0.01 mmol, 60%. Anal. Calcd for $C_{79}H_{78}P_6Pt_4S$: C, 46.8; H, 3.9. Found: C, 46.7; H, 3.4%. MS: *m/e* 1785 (P – $PtMe_3$), ^1H NMR (in $CDCl_3$): δ (ppm) = 0.14 [d, 3 H, $^3J(PH)$ = 7 Hz, $^2J(PtH)$ = 86 Hz, *Me*PtS], 0.72 [d, 3 H, $^3J(PH)$ = 7 Hz, $^2H(PtH)$ = 72 Hz, *Me*PtP], 2.03 [m, 2 H, $P_2CH^aH^b$], 3.58 [m, 1 H, $P_2CH^cH^d$], 3.89 [m, 2 H, $3J(PtH)$ = 36 Hz, $P_2CH^aH^b$], 5.58 [m, 1 H, $^2J(PH)$ = 5 Hz, $^3J(PtH)$ = 80 Hz, $P_2CH^cH^d$], 6.9–7.3 [m, 60 H, *Ph*]. $^{31}P\{^1H\}$ NMR (in CD_2Cl_2): δ (ppm) = –20.5 [t of t, 2 P, $^2J(P^aP^b)$ = 3 Hz, $^4J(P^aP^c)$ = 10 Hz, $^2J(P^aP^{a'})$ = 60 Hz, $^1J(PtP)$ = 3780 Hz, $^2J(PtP)$ = –80 Hz, $^1J(PtPt)$ = 1645 Hz, P^a], 7.3 [d of d, 2 P, $^2J(P^bP^c)$ = 65 Hz, $^4J(P^bP^{c'})$ = 25 Hz, $^2J(P^aP^b)$ = 3 Hz, $^3J(P^bP^{b'})$ = 170 Hz, $^1J(PtP^b)$ = 3300 Hz, $^2J(PtP^b)$ = 210 Hz, P^b], 14.9 [d of d of t, 2 P, $^1J(PtP^c)$ = 1960 Hz, $^3J(PtP^c)$ = 150 Hz, P^c]. $^{195}Pt\{^1H\}$ NMR (in CD_2Cl_2): δ (ppm) = –2374 [d, $^1J(PtP)$ = 1960 Hz, Pt^b], –3231 [m, $^1J(PtP^b)$ = 3300 Hz, $^1J(PtP^a)$ = 3780 Hz, $^2J(PtP^b)$ = 210 Hz, $^2J(PtP^a)$ = –80, $^3J(PtP^c)$ = 150 Hz, Pt^a].

[$Pt_4Ph_4(\mu_4$-S)(μ-dppm)$_3$] (5b). This was prepared similarly by using *cis*-[$PtPh_2(SMe_2)_2$]. Yield: 70%. Anal. Calcd for $C_{99}H_{86}P_6Pt_4S$: C, 52.3; H, 3.8. Found: C, 51.4; H, 3.5%. ^1H NMR (in $CDCl_3$): δ (ppm) = 2.1 [m, 2 H, $P_2CH^aH^b$], 3.7 [m, 1 H, $P_2CH^cH^d$], 4.0 [m, 2 H, $P_2CH^aH^b$], 5.7 [m, 1 H, $P_2CH^cH^d$], 6.9–7.5 [m, 80 H, Ph]. $^{31}P\{^1H\}$ NMR (in acetone-d_6): δ (ppm) = –15.2 [t of t, 2 P, $^2J(P^aP^b)$ = 4 Hz, $^4J(P^aP^c)$ = 8 Hz, $^2J(P^aP^{a'})$ = 60 Hz, $^1J(PtP)$ = 3880 Hz, $^2J(PtP)$ = –80 Hz, P^a], 1.1 [m, 2 P, $^1J(PtP)$ = 1800 Hz, $^3J(PtP)$ = 100 Hz, P^c], 4.6 [d of d, 2 P, $^2J(P^bP^c)$ = 65 Hz, $^4J(P^bP^{c'})$ = 25 Hz, $^2J(P^aP^b)$ = 3 Hz, $^3J(P^bP^{b'})$ = 160 Hz, $^1J(PtP)$ = 3300 Hz, $^2J(PtP)$ = 200 Hz, P^b]. $^{195}Pt\{^1H\}$ NMR (in acetone-d_6): δ (ppm) = –2574 [d, $^1J(PtP)$ = 1800 Hz, Pt^b], –3443 [m, $^1J(PtP^b)$ = 3300 Hz, $^1J(PtP^a)$ = 3880 Hz, $^2J(PtP^b)$ = 200 Hz, $^2J(PtP^a)$ = –80, $^3J(PtP^c)$ = 100 Hz, Pt^a].

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Contribution from the Departamento de Química Inorgánica,
Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009-Zaragoza, Spain

Bi- and Trinuclear PtAg Complexes with or without Pt–Ag Bonds. Molecular Structure of [$PPh_3(C_6Cl_5)ClPt(\mu$-Cl)$AgPPh_3$]

Rafael Usón,* Juan Forniés, Milagros Tomás, Irene Ara, and José M. Casas

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When $(NBu_4)_2$[*trans*-$PtCl_2(C_6Cl_5)_2$] is reacted with $O_3ClOAgL$ (L = PPh_3, PEt_3; molar ratio 1:1), the binuclear (NBu_4)[$PtAgCl_2(C_6Cl_5)_2L$] (L = PPh_3 (I), PEt_3 (II)) complexes are obtained, while, for L = PPh_2Me, the trinuclear [$Pt(C_6Cl_5)_2\{(\mu$-Cl)AgL$\}_2$] (III) is obtained in low yield. The trinuclear complexes with L = PPh_2Me (III, in higher yield), L = PPh_3 (IV), and L = PEt_3 (V) are obtained when the above-mentioned reactions are carried out in a 1:2 molar ratio. (NBu_4)[*trans*-$PtCl_2(C_6Cl_5)L$] reacts with $O_3ClOAgL'$ (molar ratio 1:1 or 1:2), yielding the novel binuclear derivatives [$L(C_6Cl_5)ClPt(\mu$-Cl)AgL′] (L′ = PPh_3, L = PPh_3 (VI), SC_4H_8 (VII), NC_5H_5 (VIII); L′ = PPh_2Me, L = PPh_3 (IX)). The structure of VI has been solved by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with a = 14.270 (2) Å, b = 14.663 (2) Å, c = 20.024 (2) Å, β = 93.58 (1)°, V = 4181.69 Å^3, and Z = 4. The structure was refined to residuals of R = 0.037 and R_w = 0.037. The "$PtCl_2(C_6Cl_5)PPh_3$" and "$AgPPh_3$" fragments are bonded by a single chlorine bridge, Pt(μ-Cl)Ag (Pt–Cl1 = 2.341 (3) Å, Ag–Cl1 = 2.514 (2) Å), and a weak Pt–Ag bond (Pt–Ag = 2.945 (1) Å), and two [$(PPh_3)(C_6Cl_5)ClPt(\mu$-Cl)$Ag(PPh_3)$] units are connected through a weak Ag′–Cl1 interaction (Ag′···Cl1 = 3.023 (2) Å). The silver atom makes a short contact with one *o*-chlorine atom of the C_6Cl_5 groups (Ag···Cl7 = 3.041 (4) Å).

Introduction

We have recently reported[1] the synthesis, structure, and reactivity of $\{(NBu_4)[Pt(C_6Cl_5)_2(\mu$-$Cl)_2Ag]\}_x$. The polymeric anion in this complex consists of trans-planar $PtCl_2(C_6Cl_5)_2$ units that lie on a pair of parallel planes and are linked by a central ribbon of silver atoms diagonally coordinated to two chlorine atoms, one on each plane. The long Pt–Ag distance (3.203 (1) Å) excludes any significant Pt–Ag bond, but each Ag atom interacts with four *o*-Cl atoms, since the C_6Cl_5 groups are so positioned as to bridge two adjacent silver atoms, thus completing around each silver atom a rhombically distorted octahedron of Cl atoms.

A dichloromethane suspension of this polymeric complex reacts[1] with group 15 ligands (L; Pt:L = 1:1) to give anionic binuclear (NBu_4)[$PtAgCl_2(C_6Cl_5)_2L$] (A) or neutral trinuclear [$Pt(C_6Cl_5)_2\{(\mu$-Cl)AgL$\}_2$] (B) complexes, depending on the neutral ligand L. The structure of one complex of each type has been established by X-ray diffraction, and in the binuclear complex (NBu_4)[$PtAgCl_2(C_6Cl_5)_2PPh_3$] (A),[1] the silver atom displays a bond to the platinum atom, which is singly bridged by a chloride ligand, and two short contacts to *o*-Cl atoms of the C_6Cl_5 groups (see Figure 1A). In the trinuclear compound [$Pt(C_6Cl_5)_2\{(\mu$-Cl)$Ag(PPh_2Me)\}_2$] (Figure 1B)[1] the absence of a Pt–Ag bond and *o*-Cl–Ag contacts is compensated by strong Ag–Cl and Ag–P bonds.

Since the insolubility of the polymeric starting complex precludes any meaningful change of the reaction conditions, it should be worthwhile to search for other synthetic approaches in order to ascertain whether both types of complexes would be accessible in all cases by a suitable choice of the molar ratio with soluble precursors. Both types of complexes (Figure 1) can be considered as the result of the interaction of a trans-planar "$PtCl_2(C_6Cl_5)_2$" fragment with one (binuclear species) or two (trinuclear species) "Ag–L" fragments. Therefore, in the present paper we study the 1:1 and 1:2 reactions between $(NBu_4)_2$[*trans*-$PtCl_2(C_6Cl_5)_2$] and $O_3ClOAgL$ (L = PPh_3, PPh_2Me, PEt_3) as well as similar reactions of the anionic (NBu_4)[*trans*-$PtCl_2(C_6Cl_5)L$] with $O_3ClOAgL'$, which give a novel type of complex, as shown by the structure of the complex with L = PPh_3 and L′ = PPh_3 that has been

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[1] Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. *Inorg. Chem.* **1986**, *25*, 4519.

Table I. Analytical, Conductivity, and Melting Point Data and Yields for Complexes I–VIII

	anal. found (calcd), %				Λ_M, Ω^{-1} cm^2 mol^{-1}	mp, °C	yield, %
	C	H	N	Cl			
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PPh_3)]$ (I)	39.91 (40.01)	3.43 (3.70)	1.06 (1.01)	30.33 (30.88)	83.6	116 dec	77
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PEt_3)]$ (II)	33.29 (33.09)	4.13 (4.13)	1.22 (1.13)	34.49 (34.50)	80.8	97 dec	73
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_2Me)\}_2$ (III)	32.73 (33.03)	2.13 (1.88)		31.10 (30.81)		114 dec	77
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_3)\}_2$ (IV)	38.17 (38.31)	2.25 (2.01)		28.54 (28.26)		137 dec	76
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PEt_3)\}_2$ (V)	23.53 (23.70)	2.36 (2.46)		34.24 (34.50)		108 dec	51
$(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VI)	43.79 (43.95)	2.71 (2.61)		21.15 (21.62)	9.9	182 dec	72
$(SC_4H_8)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VII)	34.75 (34.54)	2.49 (2.36)		26.12 (25.49)	5.9	135 dec	68
$(NC_5H_5)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VIII)	35.85 (36.11)	2.18 (2.07)	1.45 (1.45)	25.08 (25.73)	9.7	153	79
$(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_2Me)$ (IX)	40.67 (40.94)	2.59 (2.60)		23.03 (22.86)	9.4	146 dec	82

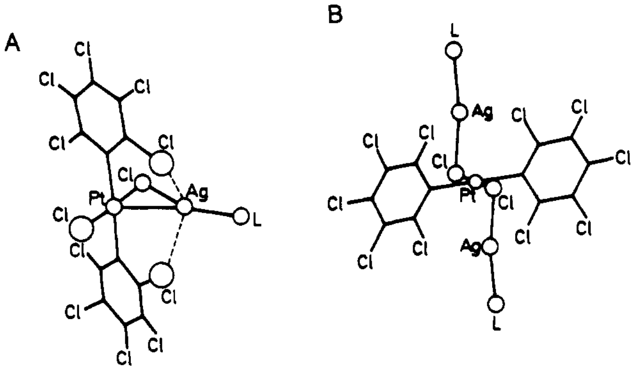

Figure 1. Schematic representations of the structures of (A) the anion $[PtAgCl_2(C_6Cl_5)_2L]^-$ (L = PPh_3, PEt_3, $AsPh_3$, $SbPh_3$) and (B) $Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)AgL\}_2$ (L = PPh_2Me, PPh_2Et, $PPhMe_2$).

Table II. Crystallographic Data for $(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$

chem formula: $PtAgCl_7P_2C_{42}H_{30}$	$T = 21 \pm 0.3$ °C
fw: 1147.779	$\lambda = 0.71073$ Å
space group: $P2_1/n$	$\rho_{calcd} = 1.82$ g cm^{-3}
$a = 14.270$ (2) Å	$\mu = 41.71$ cm^{-1}
$b = 14.663$ (2) Å	transmissn coeff: 0.3474–0.5042
$c = 20.024$ (2) Å	$R(F_0) = 0.037$
$\beta = 93.58$ (1)°	$R_w(F_0) = 0.037$
$V = 4181.71$ Å^3	
$Z = 4$	

established by a single-crystal X-ray diffraction study.

Experimental Section

The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Chlorine analyses were made as described by White,[2] a few milligrams of sucrose being added to facilitate combustion.[3] IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (4000–200 cm^{-1}) using Nujol mulls between polyethylene sheets. Molecular weights were determined with a Knauer 1100 vapor-pressure osmometer. Conductivities were measured in approximately 5×10^{-4} M acetone solution with a Philips PW 9501/01 conductometer. $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$,[4] $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)(PPh_3)]$,[5] and $O_3ClOAgL$ (L = PPh_3, $PMePh_2$, PEt_3)[6] were prepared as described elsewhere. All the reactions were carried out with exclusion of light.

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

(a) Reaction of $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ with $O_3ClOAgL$ (L = PPh_3, $PMePh_2$, PEt_3; Molar Ratio 1:1). i. L = PPh_3. To a CH_2Cl_2 (20 mL) solution of $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ (0.21 g, 0.1681 mmol) was added $O_3ClOAgPPh_3$ (0.0789 g, 0.1681 mmol), and the mixture was stirred at room temperature for 1 h. The resulting solution was evaporated to dryness, and the residue was treated with cold (0 °C) MeOH (10 mL), filtered, and washed with MeOH, giving I, yield 77%.

ii. L = PEt_3. Complex II was obtained similarly, by reacting $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ (0.15 g, 0.12 mmol) with a CH_2Cl_2 solution containing $O_3ClOAgPEt_3$ prepared from $ClAgPEt_3$ (0.0345 g, 0.132 mmol) and $AgClO_4$ (0.0547 g, 0.264 mmol); yield 74%.

iii. L = PPb_2Me. To a solution of $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ (0.2 g, 0.16 mmol) in 20 mL of CH_2Cl_2 was added $O_3ClOAgPPh_2Me$ (0.0652 g, 0.16 mmol), and the mixture was stirred at room temperature for 1 h. After filtration, the resulting solution was evaporated to dryness and the residue was treated with MeOH (15 mL) so that a yellow solid, which was identified as $[Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_2Me)\}_2]$ (III, 39% yield) was obtained. The MeOH solution was evaporated to dryness and treated with MeOH. The residue was identified as the starting material $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$.

(b) Reaction of $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ with $O_3ClOAgL$ (L = PPb_3, PPh_2Me, PEt_3; Molar Ratio 1:2). i. L = PPh_3. $O_3ClOAgPPh_3$ (0.0475 g, 0.1012 mmol) was added to a CH_2Cl_2 (15 mL) solution of $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ (0.0632 g, 0.0506 mmol), and the mixture was stirred at room temperature for 2 h. After evaporation to dryness, the residue was treated with MeOH (20 mL), filtered, and washed with MeOH, giving the pale yellow solid $[Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_3)\}_2]$ (IV) in 76% yield.

ii. L = PEt_3. Complex V was prepared similarly from $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ (0.2 g, 0.16 mmol) and $O_3ClOAgPEt_3$ (0.32 mmol).

iii. L = PPh_2Me. $(NBu_4)_2[$*trans*-$PtCl_2(C_6Cl_5)_2]$ (0.05 g, 0.04 mmol) reacts with $O_3ClOAgPPh_2Me$ (0.0326 g, 0.08 mmol) under conditions similar to those described in part (a)iii, giving III (0.041 g, 73% yield).

(c) Reaction of $(NBu_4)[PtAgCl_2(C_6Cl_5)_2PPh_3]$ (I) with $O_3ClOAgPPh_3$. To a solution of I (0.115 g, 0.0834 mmol) in CH_2Cl_2 (15 mL) was added $O_3ClOAgPPh_3$ (0.0392 g, 0.0834 mmol), and the mixture was stirred at room temperature for 1 h. The resulting solution was evaporated to dryness, and the residue was treated with MeOH (15 mL), filtered, and washed with MeOH, giving VI, yield 75%.

(d) Reaction of $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)L]$ with $O_3ClOAgL'$ (Molar Ratio 1:1).

i. L = PPh_3, L′ = PPh_3. To a CH_2Cl_2 (20 mL) solution of $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)(PPh_3)]$ (0.1 g, 0.098 mmol) was added $O_3ClOAgPPh_3$ (0.046 g, 0.098 mmol), and the mixture was stirred at 0 °C for 30 min. The resulting solution was evaporated to dryness, and the residue was treated with isopropyl alcohol (10 mL). The yellow solid obtained (VI) was washed with *n*-hexane; yield 72%.

ii. L = SC_4H_8, L′ = PPh_3; L = NC_5H_5, L′ = PPh_3; L = PPh_3, L′ = PPh_2Me. Complexes VII–IX were prepared similarly: VII, $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)(SC_4H_8)]$ (0.15 g, 0.177 mmol) and $O_3ClOAgPPh_3$ (0.0832 g, 0.177 mmol); VIII, $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)(NC_5H_5)]$ (0.1 g, 0.1194 mmol) and $O_3ClOAgPPh_3$ (0.056 g, 0.1194 mmol); IX, $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)(PPh_3)]$ (0.1 g, 0.098 mmol) and

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Table III. Selected Fractional Atomic Coordinates ($\times10^4$) and Isotropic Thermal Parameters and Their Estimated Standard Deviations for $(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$

	x	y	z	B(eq), Å^2
Pt	10108 (1)	1803 (1)	1351 (1)	7.23 (6)
Ag	8944 (1)	872 (1)	293 (1)	8.43 (13)
Cl1	10658 (2)	686 (2)	636 (1)	6.57 (35)
Cl2	9666 (3)	3031 (2)	1979 (1)	11.81 (48)
C1	10653 (9)	2728 (8)	724 (6)	8.8 (19)
C2	11584 (9)	3002 (7)	845 (6)	7.9 (17)
C3	12011 (9)	3659 (10)	453 (7)	12.4 (21)
C4	11511 (10)	4070 (9)	−63 (7)	8.8 (21)
C5	10551 (10)	3851 (8)	−206 (5)	10.7 (19)
C6	10151 (8)	3196 (8)	189 (5)	8.8 (17)
Cl3	12279 (2)	2458 (3)	1448 (2)	12.34 (58)
Cl4	13167 (3)	3957 (3)	614 (2)	12.03 (64)
Cl5	12013 (3)	4899 (3)	−540 (2)	14.86 (79)
Cl6	9900 (3)	4400 (2)	−834 (2)	16.48 (63)
Cl7	8988 (2)	2910 (2)	16 (2)	11.96 (51)
P1	9656 (2)	772 (2)	2159 (1)	8.70 (44)
P2	7304 (2)	597 (2)	98 (1)	6.90 (39)

$O_3ClOAgPPh_2Me$ (0.04 g, 0.098 mmol). Yields are given in Table I.

(e) Preparation of Crystals for X-ray Studies. Crystals of complex VI were obtained by slow diffusion (ca. 1 week at −30 °C) of *n*-hexane into a solution of the complex in CH_2Cl_2.

(f) X-ray Structure Analysis of [(PPh$_3$)(C$_6$Cl$_5$)ClPt(μ-Cl)Ag(PPh$_3$)] (VI). A yellow crystal (approximate dimensions 0.35 × 0.2 × 0.1 mm) was mounted on a Siemens/STOE AED2 automated four-circle diffractometer. Graphite-monochromated Mo Kα (λ = 0.71073 cm^{-1}) radiation was used. Accurate lattice parameters were determined by measuring the center of typically 44 reflections (25° < 2θ < 30°) including Friedel pairs. The crystal data are summarized in Table II. The intensity data were collected by the ω–2θ scan technique at room temperature. Three check reflections were measured every 45 min. They showed an average loss of intensity of 24% during the data collection time. Interpolative decay correction was applied. Data reduction included an absorption correction (ψ-scan method, 10 reflections). Minimum and maximum transmission factors were 0.3474 and 0.5042, respectively.

The positions of the platinum and silver atoms were determined from the Patterson map. The remaining atoms were located in succesive difference Fourier syntheses. All atoms were refined with anisotropic temperature factors. The weighting scheme was $w^{-1} = \sigma^2(F_o) + g(F_o^2)$ with g = 0.000771.

The final R factors are R = 0.037 and R_w = 0.037. Final atomic coordinates are given in Table III. The SHELX program package[7] was used in the determination of the structure.

Results

(a) Reaction of (NBu$_4$)$_2$[*trans*-PtCl$_2$(C$_6$Cl$_5$)$_2$] with O$_3$ClOAgL (L = PPh$_3$, PEt$_3$, PPh$_2$Me). The 1:1 reaction between $(NBu_4)_2$[*trans*-$PtCl_2(C_6Cl_5)_2$] and $O_3ClOAgL$ (L = PPh_3, PEt_3; room temperature; dichloromethane solution, 60 mL), followed by evaporating to dryness and washing with MeOH, renders pale yellow solids that are identical with those previously obtained[1] by starting from the polymeric $(NBu_4)_x[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]_x$ as indicated by the analytical data (C, H, N) and IR spectra (eq 1; structure given in Figure 1A).

$$(NBu_4)_2[PtCl_2(C_6Cl_5)_2] + O_3ClOAgL \rightarrow (NBu_4)ClO_4 + (NBu_4)[PtAgCl_2(C_6Cl_5)_2L] \quad (1)$$

L = PPh$_3$ (I), PEt$_3$ (II). Under similar conditions $O_3ClOAgPPh_2Me$ behaves differently (eq 2), and after evaporation to dryness and washing with MeOH the neutral trinuclear $[Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_2Me)\}_2]$ (III) is obtained (39% yield; structure in Figure 1B); approximately half of the starting $(NBu_4)_2$[*trans*-$PtCl_2(C_6Cl_5)_2$] can be recovered from the MeOH solution.

$$2(NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2] + 2O_3ClOAgPPh_2Me \rightarrow 2(NBu_4)ClO_4 + [Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_2Me)\}_2] + (NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2] \quad (2)$$

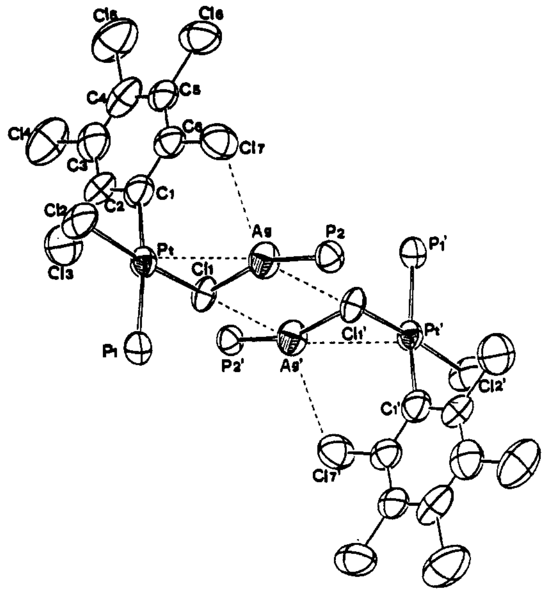

Figure 2. ORTEP drawing of $(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$. Phenyl rings of the PPh_3 group have been omitted for clarity.

The trinuclear derivatives can be obtained when the reactions between $(NBu_4)_2$[*trans*-$PtCl_2(C_6Cl_5)_2$] and $O_3ClOAgL$ are carried out in a 1:2 molar ratio (eq 3).

$$(NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2] + 2O_3ClOAgL \rightarrow 2(NBu_4)ClO_4 + [Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)AgL\}_2] \quad (3)$$

L = PPh$_2$Me (III), PPh$_3$ (IV), PEt$_3$ (V). As expected, the trinuclear complex IV can also be obtained by reacting the binuclear $(NBu_4)[Cl_2(C_6Cl_5)_2PtAgPPh_3]$ (I) with $O_3ClOAgPPh_3$ (molar ratio 1:1).

Analytical, conductivity, and melting point data for complexes I–V are given in Table I. Complexes III–V are not soluble enough in chloroform or acetone to permit a molecular weight determination.

The structures of complexes I and III have previously been established by X-ray diffraction.[1] Table IV lists significant IR absorptions. The presence of only one absorption due to the X-sensitive mode of C_6Cl_5[8] and one absorption assignable to ν(M–C)[9] indicates that both C_6Cl_5 groups are mutually trans.

Complexes I and II show two absorptions due to ν(Pt–Cl), in accordance with the presence of both terminal and bridging chloride ligands, while complexes III–V exhibit only one absorption due to their bridging Cl ligands.

(b) Reaction of (NBu$_4$)[*trans*-PtCl$_2$(C$_6$Cl$_5$)L] with O$_3$ClOAgL′. Complexes of the type (NBu_4)[*trans*-$PtCl_2(C_6Cl_5)L$], which we have prepared recently,[5] owing to their anionic nature may have an excess of electron density on the central Pt atom and may act as donors to a silver central atom in suitable complexes, thereby forming direct Pt→Ag bonds. Moreover, the presence of two Cl terminal ligands attached to the platinum center could enhance the stability of polynuclear species through additional bridging Pt(μ-Cl)Ag bonds. Therefore, to ascertain whether any chemical or structural differences would arise using a very similar but monoanionic derivative, we have studied the 1:1 and 1:2 reactions of (NBu_4)[*trans*-$PtCl_2(C_6Cl_5)L$] with $O_3ClOAgL'$. However, only the 1:1 reactions lead to novel types of neutral binuclear derivatives (VI–IX; eq 4), which are also the isolated products, when an excess of $O_3ClOAgL'$ is used. The formation of trinuclear derivatives (1:2 ratio) has not been observed.

$$(NBu_4)[PtCl_2(C_6Cl_5)L] + O_3ClOAgL' \rightarrow [LCl(C_6Cl_5)Pt(\mu\text{-}Cl)AgL'] + (NBu_4)ClO_4 \quad (4)$$

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Table IV. Relevant IR Absorptions (cm^{-1})

	C_6Cl_5[8]		
	X-sensitive	ν(Pt–C)	others
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PPh_3)]$ (I)	825 (s)	600 (m)	1226 (m), 667 (s)
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PEt_3)]$ (II)	825 (s)	600 (m)	1227 (m), 665 (s)
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_2Me)\}_2$ (III)	825 (s)	602 (m)	1227 (m), 667 (s)
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PEt_3)\}_2$ (IV)	827 (s)	602 (s)	1223 (m), 668 (s)
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_3)\}_2$ (V)	831 (m)	603 (m)	1224 (m), 666 (s)
$(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VI)	839 (m)	620 (m)	1227 (m), 671 (s)
$(SC_4H_8)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VII)	842 (m)	631 (s)	1228 (m), 673 (s)
$(NC_5H_5)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VIII)	845 (m)	627 (s)	1220 (s), 669 (s)
$(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PMePh_2)$ (IX)	832 (m)	620 (m)	1223 (m), 665 (s)

	ν(Pt–Cl)	L
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PPh_3)]$ (I)	333 (m), 298 (w)	1097 (s), 747 (s), 708 (s), 692 (s), 520 (s), 500 (s, sh)
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PEt_3)]$ (II)	325 (w), 300 (m)	1037 (m), 768 (m), 630 (m)
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_2Me)\}_2$ (III)	310 (m)	990 (s), 740 (s), 690 (s), 500 (s), 474 (m), 440 (m)
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PEt_3)\}_2$ (IV)	312 (m)	1040 (s), 767 (s), 753 (s), 695 (w)
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_3)\}_2$ (V)	313 (m)	1093 (s), 742 (s), 746 (s), 706 (s), 690 (s), 517 (s), 497 (s), 488 (s)
$(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VI)	340 (s), 317 (m)	1097 (vs), 745 (vs), 696 (vs), 529 (vs), 523 (vs), 507 (s, sh), 491 (s)
$(SC_4H_8)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VII)	319 (s, br)	1095 (vs), 746 (vs), 693 (vs), 518 (s), 505 (s), 496 (s)
$(NC_5H_5)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VIII)	320 (s), 309 (s)	1600 (s), 1092 (vs), 1068 (s), 757 (s), 750 (s), 741 (vs), 689 (vs), 640 (s), 514 (s), 498 (s), 486 (s)
$(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PMePh_2)$ (IX)	334 (s), 309 (m)	1096 (s), 900 (s), 882 (s), 742 (vs, sh), 734 (s), 711 (s), 692 (vs, sh), 530 (s), 509 (s), 492 (s)

Table V. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$

Ag–Pt	2.945 (0.001)	Cl1–Pt	2.341 (0.003)
Cl2–Pt	2.306 (0.003)	C1–Pt	2.036 (0.012)
P1–Pt	2.334 (0.003)	Cl1–Ag	2.514 (0.002)
Cl7–Ag	3.041 (0.004)	P2–Ag	2.382 (0.003)
Cl1′–Ag	3.023 (0.002)	C2–C1	1.395 (0.018)
C6–C1	1.426 (0.016)	C3–C2	1.405 (0.018)
Cl3–C2	1.712 (0.012)	C4–C3	1.361 (0.019)
Cl4–C3	1.717 (0.014)	C5–C4	1.419 (0.020)
Cl5–C4	1.728 (0.014)	C6–C5	1.389 (0.016)
Cl6–C5	1.717 (0.012)	Cl7–C6	1.725 (0.012)
Cl1–Pt–Ag	55.4 (0.1)	Cl2–Pt–Ag	126.4 (0.1)
Cl2–Pt–Cl1	172.9 (0.1)	C1–Pt–Ag	94.9 (0.3)
C1–Pt–Cl1	86.2 (0.3)	C1–Pt–Cl2	86.8 (0.3)
P1–Pt–Ag	91.8 (0.1)	P1–Pt–Cl1	95.1 (0.1)
P1–Pt–Cl2	91.7 (0.1)	P1–Pt–C1	172.6 (0.3)
Cl1–Ag–Pt	50.0 (0.1)	Cl7–Ag–Pt	70.0 (0.1)
Cl7–Ag–Cl1	97.2 (0.1)	P2–Ag–Pt	134.5 (0.1)
P2–Ag–Cl1	162.8 (0.1)	P2–Ag–Cl7	99.7 (0.1)
Cl1′–Ag–P2	89.5 (0.1)	Pt–Ag–Cl1′	132.3 (0.1)
Ag–Cl1–Ag′	97.5 (0.1)	Ag–Cl1–Pt	74.6 (0.1)

L′ = PPh_3, L = PPh_3 (VI), SC_4H_8 (VII), NC_5H_5 (VIII); L′ = PPh_2Me, L = PPh_3 (IX). Analytical and conductivity data, melting points, and yields for complexes VI–IX are given in Table I. The molecular weights of complexes VI–IX have not been determined since, although very dilute $CHCl_3$ solutions (ca. 5 × 10^{-3} *m*) can be obtained, decomposition takes place during the time required for these measurements. The structure of complex VI has been established by single-crystal X-ray diffraction studies.

Significant IR absorption frequencies for complexes VI–IX are listed in Table IV. One absorption due to the X-sensitive mode of the C_6Cl_5 group and another one due to ν(M–C)[9] are in agreement with the presence of only one C_6Cl_5 group in the complexes. Two absorptions assignable to ν(Pt–Cl) are observed for complexes VI, VIII, and IX, due to the presence of Pt–Cl terminal and Pt–Cl–Ag bonds, but complex VII shows only one broad absorption at 319 cm^{-1}.

Discussion

Structure of $[(Ph_3P)Cl(C_6Cl_5)Pt(\mu\text{-}Cl)Ag(PPh_3)]$ (VI). Crystal data collection details, atomic coordinates, and selected bond distances and angles for complex VI are given in Tables II, III, and V, respectively. The structure is shown in Figure 2. Two $[(Ph_3P)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)]$ units, which are related through a center of symmetry, are connected through weak (3.023 (2) Å) Ag′···Cl1 interactions, and each of these two units is formed by the moieties "$PtCl_2(C_6Cl_5)PPh_3$" and "$AgPPh_3$" mutually bonded by a single chlorine bridge, Pt(μ-Cl)Ag, between the metal centers (Pt–Cl1 = 2.341 (3) Å; Ag–Cl1 = 2.514 (2) Å) and possibly by a weak Pt–Ag bond (Pt–Ag = 2.945 (1) Å).

The Pt atom displays a distorted-square-planar environment formed by two chlorine atoms, one C_6Cl_5 group, and one PPh_3 molecule. Both chlorine atoms as well as the C_6Cl_5 and PPh_3 ligands are in trans positions, as in the starting material. Angles between Pt-cis-ligand bonds are in the range 86.2 (3)–95.1 (1)°, and angles between Pt-trans-ligand bonds are 172.9 (1) and 172.6 (3)°, respectively. The Pt–Cl terminal distance is shorter (Pt–Cl2 = 2.306 (3) Å) than the Pt–Cl bridging one (Pt–Cl1 = 2.341 (3) Å), as occurs in complex I, which also contains Pt–Cl terminal and Pt–Cl–Ag bridging bonds. The Pt–C1 distance is 2.036 (12) Å in the same range found for Pt–C distances in complex I, while the Pt–P1 distance is 2.334 (3) Å. The silver atom is bonded to the P atom of the PPh_3 (Ag–P = 2.382 (3) Å) and also displays a strong Ag–Cl bridging bond (Ag–Cl1 distance 2.514 (2) Å) and one weak Pt···Ag bond (Pt···Ag distance 2.945 (1) Å). the Pt–Cl1–Ag angle is 74.6 (1)°, not so acute as the Pt–Cl–Ag angle in complex I (Figure 1A), in accordance with a longer Pt···Ag distance in complex VI than in complex I. Angles around the silver atom are Pt–Ag–P2 = 134.5 (1)° and Cl1–Ag–P = 162.8 (1)°.

Moreover, as for other Pt–Ag complexes containing perhalophenyl groups, the Ag atom has a contact with one *o*-chlorine atom of the C_6Cl_5 group (Ag···Cl7 = 3.041 (4) Å) slightly longer than the *o*-Cl···Ag contacts observed in complex I. As we have described

Table VI. Comparison of Distances and Angles for Polynuclear Pentachlorophenyl Platinum–Silver Compounds

	distances, Å			angles, deg		
	Pt–Ag	Cl–Ag	Ag–P	Pt–Cl–Ag	Pt–Ag–P	Cl–Ag–P
$(NBu_4)[PtAgCl_2(C_6Cl_5)_2(PPh_3)]$ (I, A[a])	2.782 (3)	2.667 (3)	2.395 (2)	67.24 (6)	163.42 (8)	118.74 (9)
$(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)$ (VI)	2.945 (1)	2.514 (2)	2.382 (3)	71.6 (1)	134.5 (1)	162.8 (1)
$Pt(C_6Cl_5)_2\{(\mu\text{-}Cl)Ag(PPh_2Me)\}_2$ (III, B[a])	3.131 (1)	2.418 (2)	2.370 (2)	82.63 (5)		163.09 (5)

[a] Refers to part A or B of Figure 1.

elsewhere,[10] these contacts imply donation of electron density to the silver atom. Finally, two $[(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(PPh_3)]$ units are arranged in such a way that the bridging Cl1 atom of each unit is located at 3.023 (2) Å from the silver atom of the other unit, making a contact similar to that presented by the *o*-chlorine atom of the C_6Cl_5 groups. The distance between the silver atoms is 4.176 (2) Å, excluding any bonding interaction. Unfortunately, the low stability of these complexes in solution does not allow a molecular weight determination in order to establish if this weak interaction Cl1···Ag′ can be detected in solution. As for complex I and complex III, the formation of VI is the result of the interaction of two fragments, the platinum "$PtCl_2(C_6Cl_5)PPh_3$" and silver "$AgPPh_3$" moieties. However, some differences in the interactions of these moieties can be observed when the structures of the three complexes are compared. Table VI collects the main bond distances and angles. As may be seen, the interaction between the platinum and silver fragments is in the case of the anion in complex I mainly due to the Pt–Ag bond, with a very weak Pt–Cl–Ag bond, and two *o*-Cl···Ag contacts of the pentachlorophenyl groups. The interaction in the case of complex III is only due to the Pt–Cl–Ag bond, and neither Pt–Ag bonds nor *o*-Cl···Ag′ contacts are present. However, in complex VI the interaction between both fragments shows weaker Pt–Ag and stronger Pt–Cl–Ag bonds than in III. Moreover, in VI two contacts Ag···Cl, one to the *o*-Cl atom of the C_6Cl_5 group and the other to the bridging Cl1′, are detected.

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Supplementary Material Available: A full list of crystal data collection and refinement parameters, tables of bond distances and angles, anisotropic displacement parameters, and positional parameters, and a figure with the complete labeling scheme (6 pages); a table of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, Louisiana State University,
Baton Rouge, Louisiana 70803-1804, and Washington University, St. Louis, Missouri 63130

Preparation, Structure, and Redox Activity of Nickel(II), Palladium(II), and Copper(II) Cofacial Binuclear Bis(β-keto enamine) Complexes[§]

Julie R. Bradbury,[†] Jacqueline L. Hampton,[†] Daniel P. Martone,[‡] and Andrew W. Maverick*[,‡]

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The synthesis of the new bis(β-keto enamine) ligand $BBIH_2$, or 5-*tert*-butyl-*m*-xylylenebis(acetylacetone imine) (3,3′-[5-(1,1-dimethylethyl)-1,3-phenylenebis(methylene)]bis(4-amino-3-penten-2-one)), and the properties of three of its cofacial binuclear metal complexes are described. $Ni_2(BBI)_2 \cdot 2DMF$ ($Ni_2C_{50}H_{74}N_6O_6$; DMF = $(CH_3)_2NCHO$): monoclinic, space group $P2_1/c$ (No. 14); $a = 13.091$ (2), $b = 11.206$ (2), $c = 18.015$ (4) Å; $\beta = 95.92$ (1)°; $Z = 2$; $R = 0.049$ ($R_w = 0.062$) for 3583 reflections and 289 parameters. $Pd_2(BBI)_2 \cdot 2DMF$ ($Pd_2C_{50}H_{74}N_6O_6$): monoclinic, space group $P2_1/c$ (No. 14); $a = 13.251$ (3), $b = 11.196$ (2), $c = 17.962$ (5) Å; $\beta = 96.42$ (2)°; $Z = 2$; $R = 0.032$ ($R_w = 0.051$) for 3850 reflections and 289 parameters. $Cu_2(BBI)_2 \cdot 0.5CH_2Cl_2 \cdot H_2O$ ($Cu_2C_{44.5}H_{63}ClN_4O_5$): monoclinic, space group $C2/m$ (No. 12); $a = 26.802$ (5), $b = 9.887$ (2), $c = 9.021$ (2) Å; $\beta = 90.48$ (1)°; $Z = 2$; $R = 0.053$ ($R_w = 0.084$) for 1634 reflections and 142 parameters. $Ni_2(BBI)_2 \cdot 2DMF$ (Ni- - -Ni = 4.4305 (7) Å) and $Pd_2(BBI)_2 \cdot 2DMF$ (Pd- - -Pd = 4.3471 (4) Å) are isostructural, with the *cis-anti*-$M_2(BBI)_2$ geometric isomer stabilized by weak hydrogen bonding to the DMF oxygen atoms. The high crystallographic symmetry of the metal complex in $Cu_2(BBI)_2$ (Cu- - -Cu = 4.321 (1) Å) has prevented identification of the specific $M_2(BBI)_2$ isomer present. $Ni_2(BBI)_2$ and $Cu_2(BBI)_2$ exhibit quasireversible two-electron-oxidation waves in cyclic voltammetry (CH_2Cl_2 solution), whereas the analogous mononuclear complexes $M(acim)_2$ (acimH = 2-amino-2-penten-4-one) show only irreversible one-electron oxidation. Initial electrochemical oxidation of $Pd_2(BBI)_2$, while involving only one electron, is ca. 0.4 V easier than that of $Pd(acim)_2$. Thus, the binuclear species exhibit new types of redox processes, and their relatively rigid structure appears to lead to unusual kinetic stability.

Introduction

We have recently begun investigating the chemistry of cofacial binuclear transition-metal complexes derived from bis(β-diketone) ligands. Our objective has been to combine the reactivity and geometric features of the cofacial diporphyrins[1] with the synthetic versatility of the β-diketone ligand. We first reported the preparation and properties of the *m*-xylylene-bridged copper(II) complex $Cu_2(XBA)_2$ (**1**; see Chart I).[2] We have also shown that the 2,7-dimethylnaphthalene derivative $Cu_2(NBA)_2$ is capable of intramolecular coordination of guest molecules (G; see structure **2**) such as 1,4-diazabicyclo[2.2.2]octane (Dabco)[3] and pyrazine.[4] We have also been interested in the effects of modified metal coordination environments on the redox properties of the complexes. In analogous mononuclear systems, for example, Schiff-base complexes such as M(acen) (**3**; see Chart I) show more facile redox processes[5] than the parent acetylacetone derivatives.[6,7]

[†] Washington University.

[‡] Louisiana State University.

[§] Ligand abbreviations: acacH = 2,4-pentanedione; acimH = acetylacetone imine (4-amino-3-penten-2-one); salimH = salicylaldimine; $acenH_2$ = bis(acetylacetone)ethylenediimine (4,4′-[1,2-ethanediyldinitrilo]bis(3-penten-2-one)); $bzacenH_2$ = bis(benzoylacetone)ethylenediimine (3,3′-[1,2-ethanediyldinitrilo]bis(1-phenyl-1-buten-2-one)); $XBAH_2$ = *m*-xylylenebis(acetylacetone) (3,3′-[1,3-phenylenebis(methylene)]bis(2,4-pentanedione)); $NBAH_2$ = 2,7-naphthalenediylbis(methylene)bis(acetylacetone) (3,3′-[2,7-naphthalenediylbis(methylene)]bis(2,4-pentanedione)); $BBAH_2$ = 5-*tert*-butyl-*m*-xylylenebis(acetylacetone) (3,3′-[5-(1,1-dimethylethyl)-1,3-phenylenebis(methylene)]bis(2,4-pentanedione)); $BBIH_2$ = 5-*tert*-butyl-*m*-xylylenebis(acetylacetone imine) (3,3′-[5-(1,1-dimethylethyl)-1,3-phenylenebis(methylene)]bis(4-amino-3-penten-2-one)).

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