Synthesis and Characterization of $[Pt(CN)(AuCN)(AuPPh_3)_8](NO_3)$ and $Pt(CO)(AuPPh_3)_6(AuCN)_2$.Crystal Structure of $[Pt(CN)(AuCN)(AuPPh_3)_8](NO_3)$

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Abstract

$Pt(CN)(AuCN)(AuPPh_3)_8^+$ (1) can be prepared from $Pt(AuPPh_3)_8^{2+}$ (2) by an oxidative addition reaction with $Au(CN)_2^-$. The CO in $Pt(CO)(AuPPh_3)_8^{2+}$ cannot be replaced with CN^-, but in a slow process two PPh_3 are replaced, forming $Pt(CO)(AuCN)_2(AuPPh_3)_6$ (3). The compounds are characterized by ^{31}P, ^{13}C and ^{195}Pt NMR, FAB-MS and IR measurements. The structure of $Pt(CN)(AuCN)(AuPPh_3)_8(NO_3)$ is determined by X-ray diffraction (monoclinic, space group $P2_1/n$, a = 17.269(20), b = 29.638(17), c = 27.88(3) Å, β = 93.95(14)°, V = 14233 Å^3, Z = 4, the residuals are R = 0.063 and R_w = 0.090 for 5965 observed reflections and 467 variables Cu Kα radiation). In the metal cluster the central Pt atom is surrounded by eight Au atoms and one CN ligand in a spheroidal structure similar to that of $Pt(CO)(AgNO_3)(AuPPh_3)_8^{2+}$.

Introduction

Although in $Pt(AuPPh_3)_8^{2+}$ (2) the Pt is surrounded by eight Au atoms, it shows reactions similar to mononuclear Pt compounds. Upon the addition of an electrophile like Ag^+, 2 is converted into $Pt(Ag)(AuPPh_3)_8^{3+}$, with nucleophiles like CO and H^-, $Pt(CO)(AuPPh_3)_8^{2+}$ and $Pt(H)(AuPPh_3)_8^+$ are formed respectively [1, 2]. The reaction with Hg_2X_2 (X = NO_3 or Cl) results in $Pt(HgX)_2(AuPPh_3)_8^{2+}$ and can be classified as an oxidative addition [3]. Although the concept of an oxidation state for the Pt brings little clarity for this type of cluster compound, the coordination number as well as the number of valence electrons increases by two, as should be the case in oxidative additions. We report here about a new reaction of this category, in which 2 reacts with $Au(CN)_2^-$ to form $Pt(CN)(AuCN)(AuPPh_3)_8^+$ (1).

Experimental

Measurements

Elemental analysis were carried out in the microanalytical laboratory of this university and by Dr A. Bernhardt, Elbach über Engelskirchen, F.R.G. ^{195}Pt NMR spectra of CD_2Cl_2 solutions were recorded on a Bruker WM-200 operating at 40.0225 MHz with $PtCl_6^{2-}$ in D_2O as external reference. $^{13}C\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on the same spectrometer operating at 50.3234 and 81.961 MHz with TMS and TMP in CD_2Cl_2 as reference respectively. The infrared spectra of CsI pellets were recorded on a Perkin-Elmer 1720-x infrared Fourier transform spectrometer. Fast atom bombardment mass spectrometry (FAB-MS) measurements were carried out in the Chemistry Department of the University of Minnesota using a V.G. Analytical Ltd. 7070 E-HF high-resolution double-focussing mass spectrometer. A *meta*-nitro-benzyl matrix was used and mass calibration was achieved with reference spectra of CsI clusters [4].

Preparation of the Compounds

$[Pt(CN)(AuCN)(AuPPh_3)_8](NO_3)$ (1)

(a) To a solution of 100 mg (25.0 μmol) $Pt(AuPPh_3)_8(NO_3)_2$ in 5 ml methanol, 7.2 mg (25.0 μmol) solid $K[Au(CN)_2]$ is added, while stirring. After 5 min stirring a red precipitate is formed. The precipitate is filtered off on hyflo and redissolved in dichloromethane. Red crystals were precipitated by slow diffusion of diethyl ether in the dichloromethane solution. The red crystals were filtered off, washed with diethyl ether and dried in vacuum. Yield 100 mg (24.0 μmol).

(b) To a solution of 600 mg (150.3 μmol) $Pt(AuPPh_3)_8(NO_3)_2$ in 30 ml methanol, 20 mg (307.7 μmol) KCN in 20 ml methanol is added, while stirring. After 3 days stirring a red precipitate is formed. The precipitate is filtered off on hyflo and redissolved in dichloromethane. Red crystals were precipitated by slow diffusion of diethyl ether in the dichloromethane solution. The red crystals were

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filtered off, washed with diethyl ether and dried in vacuum. Yield 94 mg (22.5 μmol).

Anal. Calc. for $PtAu_9P_8C_{146}H_{120}N_3O_3$ (mol. wt. 4180.18): C, 41.95; H, 2.89; N, 1.01; Pt, 4.67; Au, 42.41. Found: C, 41.56; H, 2.99; N, 1.00; Pt, 5.11; Au, 42.10%. IR: in addition to the bands due to PPh_3 one band at 1360 cm^{-1} was observed which is characteristic of uncoordinated NO_3^- and two bands at 2116 and 2061 cm^{-1} which are $\nu(CN_{Au})$ and $\nu(CN_{Pt})$ respectively. ^{31}P NMR: $\delta = 50.15$ with $^2J(P-^{195}Pt)$ (doublet) = 360 Hz. ^{195}Pt NMR: $\delta = -5507.0$ with $^2J(Pt-^{31}P)$ (nonet) = 360 Hz. Conductivity in acetone at 25 °C $\Lambda_0 = 147.1$ cm^2 mol^{-1} ohm^{-1}.

[Pt(^{13}CN)(Au^{13}CN)(AuPPh$_3$)$_8$](NO$_3$)

The procedure (b) as described above, but instead of KCN, $K^{13}CN$ was used. IR: $\nu(^{13}CN_{Pt}) = 2017$ cm^{-1} and $\nu(^{13}CN_{Au}) = 2071$ cm^{-1}. ^{13}C NMR: PtCN $\delta = 132.3$ with $^1J(C-^{195}Pt)$ (doublet) = 902.8 Hz, $^3J(C-^{31}P)$ (nonet) = 7.6 Hz, $^3J(C-C)$ (doublet) = 6.8 Hz; AuCN $\delta = 166.7$ with $^2J(C-^{195}Pt)$ (doublet) = 113.5 Hz, $^3J(C-C)$ (doublet) = 6.8 Hz, $^4J(C-^{31}P)$ (nonet) ≈ 2 Hz. The $^3J(C-C)$ coupling was verified by $^{13}C\{H,^{31}P\}$ NMR.

Pt(CO)(AuPPh$_3$)$_6$(AuCN)$_2$ (3)

CO was bubbled through a solution of 236 mg (59.1 μmol) $Pt(AuPPh_3)_8(NO_3)_2$ in 10 ml methanol. The color of the solution changed from brown to red in 1 min. After 2 min stirring 7.6 mg (116.9 μmol) solid KCN was added. The reaction mixture was stirred for 48 h at room temperature. A red precipitate was formed, which was filtered off on hyflo and redissolved in dichloromethane. Red crystals were precipitated by slow diffusion of diethyl ether into the dichloromethane solution. These were filtered off, washed with diethyl ether and dried in vacuum. Yield 40.6 mg (11.8 μmol).

Anal. Calc. for $PtAu_8P_6C_{111}H_{90}N_2O$ (mol. wt. 3424.64): C, 38.93; H, 2.64; N, 0.82. Found C, 38.80; H, 2.64; N, 0.86%. IR: $\nu(CO) = 1938$ cm^{-1} and $\nu(CN_{Au}) = 2115$ cm^{-1}. ^{31}P NMR: $\delta = 52.4$ with $^2J(P-^{195}Pt)$ (doublet) = 385.6 Hz. ^{195}Pt NMR: $\delta = -5822.4$ with $^2J(Pt-^{31}P)$ (septet) = 385.7 Hz.

$Pt(AuPPh_3)_8(NO_3)_2$ and $KAu(CN)_2$ were prepared according to the literature [5, 6].

Structure Determination of Pt(CN)(AuCN)(AuPPh$_3$)$_8$(NO$_3$)

Collection and reduction of crystallographic data

Since the single crystals decomposed very quickly upon their removal from the mother liquor, a red crystal of $Pt(CN)(AuCN)(AuPPh_3)_8(NO_3)$ was mounted in a capillary together with a mixture of dichloromethane and diethyl ether. X-ray data were measured on a Nonius CAD4 diffractometer. Standard experimental details are given elsewhere [7].

TABLE 1. Crystal data for $(CN)Pt(AuPPh_3)_8(AuCN)(NO_3)$

Chemical formula	$PtAu_9P_8C_{146}H_{120}N_3O_3$
Formula weight	4076.4
a (Å)	17.269(20)
b (Å)	29.638(17)
c (Å)	27.88(3)
β (°)	93.95(14)
V (Å^3)	14233
Z	4
Space group	$P2_1/n$ (No. 14)
T (°C)	20
λ (Å)	1.541838
ρ_{calc}	(g cm^{-3}) 1.902
μ (Cu Kα)	(cm^{-1}) 194.53
$R(F_o)$	0.063
R_wF_o	0.090

The crystal data are listed in Table 1. No extinction correction was performed. Hardware problems with the CAD4 goniometer during the measurements and a cleavage of the crystal, detected after the completion of the measurements, gave a great variation in the intensities of equivalent reflections. Any set of equivalent reflections with a mean deviation greater than 0.12 times the mean intensity was skipped.

Solution and refinement of the structure

The positions of four metal atoms were found by the direct method part of SHELXS [8]. The other metal atoms were found by DIRDIF [9]. The remaining non-hydrogen atoms were positioned from successive difference Fourier maps. The structure was refined by full-matrix least-squares using SHELX [10]. The phenyl rings were treated as regular hexagons, and their hydrogen atoms are placed at ideal positions. Isotropic refinement converged to $R = 0.13$. At this stage an empirical absorption correction was applied (DIFABS) [11] resulting in a further decrease of R to 0.10. A large number of small peaks in the Fourier syntheses, found at positions between the cluster ions (at distances more than 3.5 Å from any atom), could not be interpreted unambiguously. They are ascribed to a mixture of a (disordered) NO_3^- ion and solvent molecules. Some of these peaks suggested the geometry of NO_3 or the solvent molecules, but none of them were found well enough to warrant inclusion in the refinement. During the final stage of the refinement, the anisotropic parameters of the gold, platinum and phosphorus atoms were refined. The phenyl groups were treated as rigid groups during the refinement. The hydrogen atoms were given fixed isotropic temperature factors of 0.06 Å^2. The function minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0.0008F_o^2]$. Positional and thermal parameters of selected atoms are given in Table 2, and selected bond distances and angles are provided in Table 3. The molecular structure is given in Fig. 1 [12].

Results

Synthesis and Characterization of 1

The preferred synthesis of **1** is the reaction of **2** with $Au(CN)_2^-$, which proceeds in minutes with nearly 100% yield. The reaction of **2** with KCN is slow and complicated, **1** is formed after 3 days with only 15% yield. Elemental analysis shows a composition of $PtAu_9(PPh_3)_8(CN)_2NO_3$. The infrared spectrum shows an absorption at 1360 cm^{-1} characteristic for the free uncoordinated NO_3^- ion. The conductivity measurement in acetone solution showed Λ_0 = 147.1 cm^2 mol^{-1} ohm^{-1} which is in the range for 1:1 electrolytes. We conclude that the cluster $[PtAu_9(PPh_3)_8(CN)_2]$ is a monopositive ion and the NO_3^- is the counter ion. The ^{13}C NMR spectrum of the isotopically labeled compound $[PtAu_9(PPh_3)_8(^{13}CN)_2]NO_3$ shows two CN sites, one at δ = 132.3 and a Pt–C coupling of 902.8 Hz and one at δ = 166.7 and a Pt–C coupling of 113.5 Hz. These couplings are interpreted as ^1J(Pt–C) and ^2J(Pt–C) and we conclude that one CN is bonded to Pt and the other to one of the Au atoms. The infrared spectrum shows two CN stretching

TABLE 2. Selected fractional positional and thermal parameters for $Pt(CN)(AuPPh_3)_8(AuCN)(NO_3)$

Atom	x	y	z	U_{eq} (×100)[a]
Pt	0.55275(9)	0.74948(6)	0.35494(6)	2.53(7)
Au1	0.70959(9)	0.75179(6)	0.36756(6)	3.24(8)
Au2	0.62492(10)	0.81474(7)	0.30494(6)	3.88(8)
Au3	0.49444(11)	0.83364(7)	0.35958(7)	5.13(9)
Au4	0.39724(10)	0.75529(7)	0.35411(6)	3.85(8)
Au5	0.48392(10)	0.69092(7)	0.41405(6)	3.56(8)
Au6	0.62506(9)	0.66893(6)	0.37027(6)	2.98(7)
Au7	0.47974(10)	0.77543(7)	0.26958(6)	3.61(8)
Au8	0.48333(10)	0.67981(6)	0.30608(6)	3.53(8)
Au9	0.62921(10)	0.71973(7)	0.27901(6)	3.68(8)
P1	0.8398(5)	0.7630(4)	0.3848(4)	2.0(4)
P2	0.6826(6)	0.8704(4)	0.2617(4)	3.9(5)
P3	0.4641(9)	0.9008(5)	0.3954(5)	7.5(7)
P4	0.2672(6)	0.7633(4)	0.3622(4)	4.4(5)
P5	0.4463(6)	0.6563(4)	0.4831(4)	3.9(5)
P6	0.7034(6)	0.6080(4)	0.3898(4)	3.2(5)
P7	0.4220(7)	0.7906(4)	0.1942(4)	4.3(5)
P8	0.4416(7)	0.6164(4)	0.2625(4)	2.4(5)
C1	0.5795(21)	0.7707(13)	0.4198(14)	2.1(11)
N1	0.5969(20)	0.7892(12)	0.4549(14)	9.2(12)
C2	0.6913(27)	0.7001(16)	0.2240(18)	6.1(15)
N2	0.7266(24)	0.6897(14)	0.1908(15)	12.1(15)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j a^*_i a^*_j a_i a_j U_{ij}$ in Å^2.

TABLE 3. Selected bond lengths (Å) and bond angles (°) for $Pt(CN)(AuPPh_3)_8(AuCN)(NO_3)$ (with e.s.d.s)

Pt–Au1	2.708(2)
Pt–Au2	2.734(2)
Pt–Au3	2.696(2)
Pt–Au4	2.690(2)
Pt–Au5	2.722(2)
Pt–Au6	2.714(2)
Pt–Au7	2.726(2)
Pt–Au8	2.708(2)
Pt–Au9	2.718(2)
Au1–Au2	2.883(2)
Au1–Au6	2.860(2)
Au1–Au9	2.907(2)
Au2–Au3	2.861(2)
Au2–Au7	2.876(2)
Au2–Au9	2.909(3)
Au3–Au4	2.863(3)
Au3–Au7	3.041(3)
Au4–Au5	2.886(2)
Au4–Au7	2.898(2)
Au4–Au8	3.046(2)
Au5–Au6	2.875(2)
Au5–Au8	3.027(2)
Au6–Au8	2.948(2)
Au6–Au9	2.961(2)
Au7–Au8	3.011(3)
Au7–Au9	3.060(2)
Au8–Au9	2.929(2)
Au1–P1	2.290(9)
Au2–P2	2.308(10)
Au3–P3	2.304(13)
Au4–P4	2.284(9)
Au5–P5	2.314(9)
Au6–P6	2.299(11)
Au7–P7	2.307(11)
Au8–P8	2.325(11)
Pt–C1	1.94(4)
Au9–C2	2.02(5)
C1–N1	1.14(4)
C2–N2	1.18(5)
Au1–Pt–Au2	64.0(1)
Au1–Pt–Au3	110.1(1)
Au1–Pt–Au4	171.4(1)
Au1–Pt–Au5	114.3(1)
Au1–Pt–Au6	63.7(1)
Au1–Pt–Au7	120.3(1)
Au1–Pt–Au8	119.3(1)
Au1–Pt–Au9	64.8(1)
Au2–Pt–Au3	63.6(1)
Au2–Pt–Au4	116.1(1)
Au2–Pt–Au5	173.2(1)
Au2–Pt–Au6	118.8(1)
Au2–Pt–Au7	63.6(1)
Au2–Pt–Au8	119.0(1)
Au2–Pt–Au9	64.5(1)
Au3–Pt–Au4	64.2(1)
Au3–Pt–Au5	112.4(1)
Au3–Pt–Au6	167.3(1)
Au3–Pt–Au7	68.2(1)

(continued)

TABLE 3. *(continued)*

Au3–Pt–Au8	125.2(1)
Au3–Pt–Au9	122.7(1)
Au4–Pt–Au5	64.4(1)
Au4–Pt–Au7	64.7(1)
Au4–Pt–Au6	120.4(1)
Au4–Pt–Au8	68.7(1)
Au4–Pt–Au9	123.5(1)
Au5–Pt–Au6	63.9(1)
Au5–Pt–Au7	120.9(1)
Au5–Pt–Au8	67.8(1)
Au5–Pt–Au9	121.4(1)
Au6–Pt–Au7	124.4(1)
Au6–Pt–Au8	65.9(1)
Au6–Pt–Au9	66.1(1)
Au7–Pt–Au8	67.3(1)
Au7–Pt–Au9	68.4(1)
Au8–Pt–Au9	65.3(1)
Pt–Au1–P1	171.7(3)
Pt–Au2–P2	178.4(3)
Pt–Au3–P3	156.5(4)
Pt–Au4–P4	173.4(3)
Pt–Au5–P5	161.0(3)
Pt–Au6–P6	170.0(3)
Pt–Au7–P7	174.2(3)
Pt–Au8–P8	171.8(3)
Pt–Au9–C2	176.5(13)
Pt–C1–N1	170(4)
Au9–C2–N2	178(4)
Au9–Pt–C1	115.3(0)

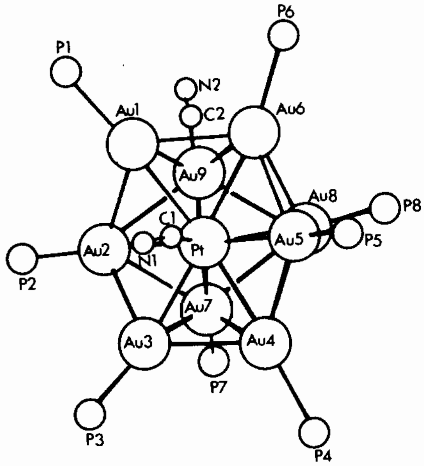

Fig. 1. X-ray structures of $Pt(CN)(AuCN)(AuPPh_3)_8(NO_3)$. Phenyl groups and the NO_3^- are omitted for the sake of clarity.

vibrations at 2116 and 2061 cm^{-1}, which upon ^{13}C labeling shift to 2071 and 2016 cm^{-1}. In 3 CN is bonded only to Au and has a CN vibration at 2115 cm^{-1}. The infrared data thus confirm the presence of a CN bonded to Au (2116 cm^{-1}) and another CN (2061 cm^{-1}) which the NMR data prove to be bonded to Pt. The ^{31}P NMR shows one P site, so we think that all phosphines are bonded to the peripheral Au atoms of the cluster, as normally found for Au phosphine cluster compounds, fluxionality shows them as a single site in the ^{31}P NMR at room temperature. The ^{195}Pt NMR data are in accord with the structure $[Pt(CN)(AuCN)(AuPPh_3)_8]^+$. Comparing these Pt NMR data with those of $Pt(CO)(AuPPh_3)_8(AgNO_3)^{2+}$, where a CN^- and a AuCN group are replaced respectively by a CO and a $AgNO_3$ group, is interesting. The similarity of the chemical shifts and ^2J(Pt–P) coupling of **1** and $Pt(CO)(AuPPh_3)_8(AgNO_3)^{2+}$, respectively $\delta = -5507.0$ (^2J(Pt–P) = 360 Hz) and $\delta = -5688.0$ (^2J(Pt–P) = 377 Hz) [2], is striking.

Fast atom bombardment mass spectrometry has been shown to be a successful technique for determining the correct molecular composition of cationic cluster compounds [4]. The positive ion of **1** in the 1000–4000 mass range has a great number of peaks; a selection of the centroids of heavy fragments is given in Table 4. The results are in good agreement with the composition and structure of the cluster as discussed above.

Synthesis and Characterization of 3

Complex **3** is formed in a slow reaction of $[Pt(CO)(AuPPh_3)_8]NO_3$ and KCN. After 2 days the yield is only 20%. The composition is indicated by elemental analysis and the presence of CO and CN is shown in the infrared spectrum which has bands at 1938 (CO) and 2115 (CN) cm^{-1}. **3** is soluble in toluene, and it gives a non-conducting solution in acetone. The ^{31}P NMR shows one singlet with Pt satellites (^2J(Pt–P) = 385.6 Hz) and the ^{195}Pt NMR shows the Pt–P coupling in a septet. These data prove that the phosphines are bonded to Au and CO is bonded to Pt like in the parent compound. Two peripheral Au atoms are then bonded to CN and the complete structure is a neutral molecule $Pt(CO)(AuPPh_3)_6(AuCN)_2$. We think that **3** is formed in a simple substitution reaction

$$Pt(CO)(AuPPh_3)_8{}^{2+} + 2CN^- \longrightarrow Pt(CO)(AuPPh_3)_6(AuCN)_2 + 2PPh_3$$

TABLE 4. Positive ion FAB-MS data of $Pt(CN)(AuCN)(AuPPh_3)_8(NO_3)$; M = $Pt(CN)(AuCN)(AuPPh_3)_8$

Mass	Calculated mass	Assignments	Relative abundance (%)
4118.2[a]	4117.40	$(M)^+$	30
3855.68	3855.31	$(M - PPh_3)^+$	50
3632.68	3632.34	$(M - Au - PPh_3\text{-}CN)^+$	100
3593.60	3593.20	$(M - 2PPh_3)^+$	60

[a] Not matched.

Discussion

The addition

$$Pt(AuPPh_3)_8{}^{2+} + Au(CN)_2{}^- \longrightarrow Pt(CN)(AuCN)(AuPPh_3)_8{}^+$$

is a fast and clean reaction in which Pt raises its coordination from 8 to 10 and the cluster-electron configuration changes from $(S^\sigma)^2(P^\sigma)^4$ into $(S^\sigma)^2(P^\sigma)^6$. In the crystalline state CN and AuCN are not in neighbouring positions, the angle NC–Pt–AuCN is 115.3°. Since the reaction is so fast in methanol solution the mechanism is probably ionic in nature. The fluxionality of clusters of this type is fast even at room temperature, so the relative positions of CN and AuCN as found in the crystalline state may not be the same as those in the primary reaction product. When 2 is allowed to react with 2 equivalents of KCN in methanol the reaction is slow and complicated, only 15% yield of 1 is formed among other unidentified products. If $Pt(CN)(AuPPh_3)_8{}^+$ is formed it could be unstable, splitting off $Au(CN)(PPh_3)$, which after conversion with CN^- into $Au(CN)_2{}^-$ could give 1. Such a combination of fragmentation and growth is also known for $Au(AuPPh_3)_x$ cluster compounds and we have detected similar reactions with 2 and Cl^-, Br^- and I^- [13]. In $Pt(CO)(AuPPh_3)_8{}^{2+}$ the Pt is blocked by the firmly bonded CO and then this reaction sequence is not possible. After some days the Au bonded phosphines are partially substituted by CN^- and 20% yield of 3 is found to be formed. The structure of 1 is similar to that of $Pt(CO)(AgNO_3)(AuPPh_3)_8{}^{2+}$. The Pt–Au distances are in the range 2.69–2.73 Å, including the Pt–AuCN distance (2.718 Å). In $Pt(CO)(AgNO_3)(AuPPh_3)_8{}^{2+}$ the Pt–Au distances are 2.69–2.79 Å. The Au–P bond lengths are 2.29–2.32 Å, which is normally found in clusters of this type. The Pt–CN bond length is 1.94 Å as compared to 1.96–2.02 Å in $Pt(CN)_4{}^{2-}$ [14] while the Au–CN bond length is 2.02 Å which is short compared to 2.12 Å in $Au(CN)_2{}^-$ [15]. The C–N bond lengths are in the normal range. The chemical reactivity of 2 is rich, with various types of reactions. Electrophilic, nucleophilic, oxidative addition, substitutions and redox reactions have now been reported. Further study is in progress.

Supplementary Material

Tables of additional temperature factors, fractional position parameters, thermal parameters, bond distances and angles (29 pages); listings of observed and calculated structure factors (29 pages) are available from the authors on request.

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