New Compounds with Platinum to Silver Bonds Unsupported by Covalent Bridges

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

*Department of Inorganic Chemistry
University of Zaragoza, Zaragoza, Spain*

F. Albert Cotton* and Larry R. Falvello

*Department of Chemistry and Laboratory for
Molecular Structure and Bonding
Texas A&M University, College Station, Texas 77843*

The chemistry of heteronuclear silver–platinum cluster complexes, containing homo- and/or heteronuclear metal–metal bonds, has been undergoing rapid development recently in our laboratories.[1,2] The use of $C_6X_5^-$ in the starting anionic platinum complexes is a critical factor in this chemistry. We have already reported[1] the preparation and structure of the compound $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6F_5)_4]$, obtained by the (1:1) reaction between $(NBu_4)_2[PtCl_2(C_6F_5)_2]$ and $AgNO_3$ (or $AgClO_4$), in which there are Pt–Ag bonds (2.772 (3) Å) and also, perhaps, weak Ag–Ag bonds (2.994 (6) Å). In several other compounds[2] we have found Pt–Ag bonds (all supported by bridging ligands), with lengths of about 2.79 Å. We now wish to report two new compounds, prepared from anionic (pentafluorophenyl)platinum precursors, in which there are Pt–Ag bonds entirely unsupported by any covalent bridging ligands.

Compound **1** $(C_4H_8S)(C_6F_5)_3PtAgP(C_6H_5)_3$, is a colorless crystalline air-stable solid,[3] prepared by reaction 1. Its structure

$$(NBu_4)[Pt(C_6F_5)_3(SC_4H_8)] + O_3ClOAgP(C_6H_5)_3 \xrightarrow{CH_2Cl_2}$$
$$NBu_4ClO_4 + [(SC_4H_8)(C_6F_5)_3PtAgP(C_6H_5)_3] \quad (1)$$
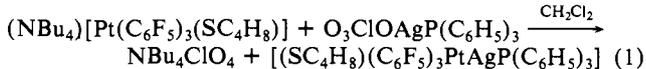
(Figure 1) has been determined.[4] There is a direct, unbridged Pt–Ag bond, which, at 2.637 (1) Å, is shorter than any previously known Pt–Ag bond. The platinum atom is coordinaed by a square array of three C_6F_5 groups and a tetrahydrothiophene molecule, with the platinum atom in the ligand–atom plane. The Pt–Ag bond is approximately perpendicular to this plane, with Ag–Pt–L angles ranging between 88° and 99°. The Pt–Ag–P angle is 174.3 (1)°.

One ortho fluorine atom of each C_6F_5 group makes a close contact with the silver atom: Ag···F(6) = 2.757 (7) Å; Ag···F(11) = 2.791 (7) Å; Ag···F(1) = 2.763 (8) Å. As before,[1] the reasons for and effects of these contacts are not obvious, but they possibly facilitate attractive forces that contribute to the stability of the molecule. The ring containing F(1) is tilted (39°) from the Pt–Ag–C(1) plane, and the C(1)–Pt–Ag angle (88°) is smaller than the other two C–Pt–Ag angles (97°, 98.5°). Hence, the Ag···F(1) distance is similar to the other two Ag···F distances. Eliminating the twist of the ring would yield a series of unacceptable contacts.[5] In summary, avoidance of repulsive contacts while maintaining three Ag···F contacts appears to account for all conformational features of this molecule.

It seems sensible to assign formal oxidation numbers of I and II to Ag and Pt, respectively, and assign a bond order of 1 to the Pt–Ag bond.[6-9] Further chemical and physical studies of this
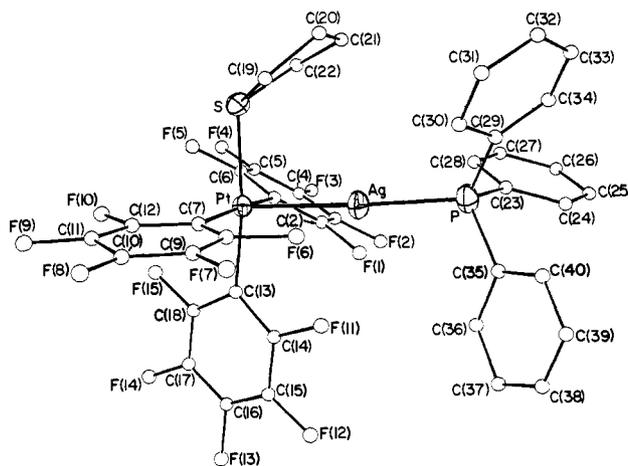
Figure 1. $(C_4H_8S)(C_6F_5)_3PtAgP(C_6H_5)_3$ molecule. All carbon and fluorine atoms are represented by arbitrarily small circles for clarity.
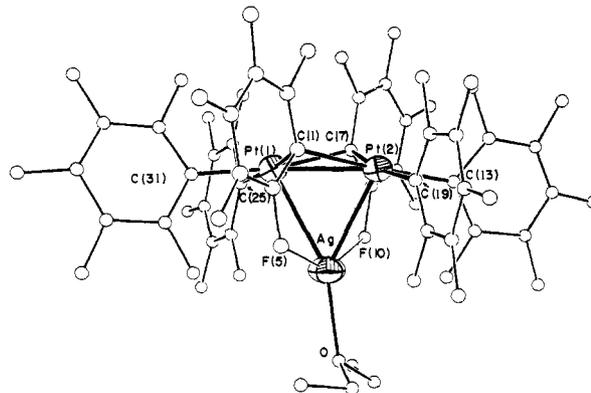
Figure 2. $[Pt_2Ag(C_6F_5)_6(Et_2O)]^-$ anion. All nonmetal atoms are represented by arbitrarily small circles for clarity.

molecule are in progress, including an NMR study of Pt, Ag, and P nuclear couplings.

Compound **2**, $(NBu_4)[Pt_2Ag(C_6F_5)_6(C_2H_5)_2O]\cdot(C_2H_5)_2O$, is a yellow solid,[10] prepared according to eq 2 and recrystallized from an ether–hexane mixture. The presence of ether is verified by ^1H NMR. The structure of the $[Pt_2Ag(C_6F_5)_6(Et_2O)]^-$ anion, determined by X-ray crystallography,[11] is shown in Figure 2.
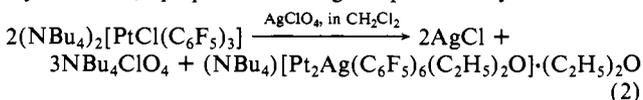
$$2(NBu_4)_2[PtCl(C_6F_5)_3] \xrightarrow{AgClO_4, \text{ in } CH_2Cl_2} 2AgCl +$$
$$3NBu_4ClO_4 + (NBu_4)[Pt_2Ag(C_6F_5)_6(C_2H_5)_2O]\cdot(C_2H_5)_2O$$
$$(2)$$

The structure of the trinuclear anion in **2** displays unusual features which make this species a challenge for bonding theory. Pairs of $Pt(C_6F_5)_3^-$ units that formally result after the abstraction of Cl^- from the starting anion are united through bridging C_6F_5 groups so that each Pt atom has roughly (see below) square-pyramidal coordination. The Pt atoms are only 2.698 (1) Å apart,

(1) Uson, R.; Forniés, J.; Tomás, M.; Cotton, F. A.; Falvello, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 2482.

(2) Several unpublished studies by the present authors.

(3) Elemental Anal. Calcd for $C_{40}H_{23}F_{15}SPAgPt$: C, 41.57; H, 1.99. Found: C, 41.79; H, 2.27.

(4) Space group: $P2_1/n$; $a = 14.006$ (2) Å, $b = 17.441$ (3) Å, $c = 17.407$ (2) Å; $\beta = 110.74$ (1)°, $Z = 4$. The structure (532 parameters) was refined to 4101 data ($4.0 \leqslant 2\theta \leqslant 50.0°$) with $F_o^2 \geqslant 3\sigma(F_o^2)$, gathered on a P3/F diffractometer. Discrepancy indices were $R = 0.0414$, $R_w = 0.0518$, and quality-of-fit = 0.95.

(5) Rotation by 39° about the Pt–C(1) bond would make the following changes in nonbonded distances (Å): Ag···F(1) from 2.76 to 2.31; C(6)···F(15) from 3.31 to 2.76; F(5)···C(18) from 4.08 to 2.82; F(5)···F(15) from 3.20 to 1.86; F(1)···P from 3.93 to 3.29; F(1)···C(23) from 3.87 to 3.12; F(1)···C(28) from 3.41 to 2.36; F(2)···C(27) from 3.96 to 2.89.

(6) Several compounds believed to have $Pt^{II}\rightarrow Ag^I$ single bonds, but also bridging ligands, were reported in 1982.[7] Their structures were assigned by analogy with some presumed Pt–Hg analogs[8] with known structures, and therefore Pt–Ag distances are not available, although Ag–Pt coupling constants (ca. 170 Hz) were reported.[9]

(7) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1982**, *21*, 2026.

(8) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.

(9) van der Ploeg, A. F. M. J.; van Koten, G.; Brevard, C. *Inorg. Chem.* **1982**, *21*, 2878.

(10) Elemental anal. Calcd for $C_{56}H_{46}NOF_{30}AgPt_2$: C, 36.98; H, 2.53; N, 0.77. Found: C, 36.98; H, 2.49; N, 0.69. Compound **2** loses one molecule of crystal ether after 30 min at 80 °C.

(11) Space group: $P2_1/n$; $a = 11.278$ (6) Å; $b = 25.643$ (8) Å; $c = 22.359$ (7) Å; $\beta = 94.92$ (3)°, $Z = 4$. The structure (779 parameters) was refined to 4048 data ($4.0 \leqslant 2\theta \leqslant 47.0°$) with $F_o^2 \geqslant 3\sigma(F_o^2)$, gathered on a CAD-4 diffractometer. Final residuals were $R = 0.0439$, $R_w = 0.0495$, and quality-of-fit = 1.17.

which would imply either that a Pt–Pt bond exists or that the spread of the bridging C_6F_5 groups (both Pt–C–Pt angles = 74.1°) forces the two Pt atoms to this distance. This is the first case in which a C_6F_5 group has been proved to act as a bridging ligand, but some complexes containing bridging phenyl groups have been structurally characterized.[12] In addition, the Pt–Ag distances, 2.827 (2) and 2.815 (2) Å, together with the fact that there are no ligands serving as bridges across the Pt–Ag edges of the Pt_2Ag triangle, imply that there are also Pt–Ag bonds. Of course, fractional bond orders may well prevail in the Pt–Pt and Pt–Ag bonds. If the Pt and Ag atoms are assigned formal oxidation numbers of II and I, respectively, a total of four electrons would be available for the set of metal–metal bonds.

There are close approaches of ortho F atoms (from the bridging groups) to the silver atom: Ag···F(5), 2.66 (1) Å; Ag–F (10), 2.67 (1) Å. The Pt–C distances to the terminal C_6F_5 groups are 2.02 and 2.06 Å. The Pt–C_{bridge} distances are longer, but they are distinctly unequal (C(1)–Pt(1), 2.28 (2) Å; C(1)–Pt(2), 2.19 (2) Å; C(7)–Pt(1), 2.20 (2) Å; C(7)–Pt(2), 2.28 (2) Å), so that each Pt–C–Pt unit is unsymmetrical. Each C_6F_5 bridging group is practically perpendicular to the Pt_2Ag plane, with dihedral angles of 96.7° and 98.3°. The dihedral angle between Pt(1)–C(1)–Pt(2) and Pt(1)–C(7)–Pt(2) is 30.0°.

Supplementary Material Available: Tables of atomic positional parameters for both structures (7 pages). Ordering information is given on any current masthead page.

(12) Malone, J. F.; McDonald, N. S. *J. Chem. Soc., Chem. Commun.* **1967**, 444. Bradford, C. W.; Nyholm, R. S.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1972**, 87.

Selectivity and Charge Transfer in Photoreactions of α,α,α-Trifluorotoluene with Olefins[†]

Jochen Mattay,* Jan Runsink, Thomas Rumbach, Cuong Ly, and Joachim Gersdorf

Institut für Organische Chemie der RWTH Aachen Prof.-Pirlet-Str. 1, D-5100 Aachen, West Germany

We have recently shown that charge transfer may influence the selectivity of product formation in various bimolecular photoreactions.[1,2] In extension of these investigations we have studied the photoreactions of α,α,α-trifluorotoluene (1) with the olefins 2 and 6 and we have found striking changes in the mode of reaction.[3] In this paper we wish to present the first example of C–F bond breakage of α-fluorinated alkyl arenes during a photoaddition reaction.[4-7] Furthermore the change of reactivity will

[†] Part 5 of "Selectivity and Charge Transfer in Photoreactions of Donor-Acceptor Systems"; for part 4, see ref 1d.
(1) (a) Mattay, J.; Gersdorf, J.; Santana, I. J. *J. Photochem.* **1983**, *23*, 319. (b) Mattay, J.; Gersdorf, J.; Leismann, H.; Steenken, S. *Angew. Chem.* **1984**, *96*, 240; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 249. (c) Mattay, J.; Gersdorf, J.; Freudenberg, U. *Tetrahedron Lett.* **1984**, 817. (d) Gersdorf, J.; Mattay, J. *J. Photochem.*, in press.
(2) Leismann, H,; Mattay, J.; Scharf, H.-D. *J. Am. Chem. Soc.* **1984**, *106*, 3985.
(3) The results have been partly presented: Mattay, J.; Runsink, J.; Rumbach, T.; Ly, C.; Gersdorf, J. *Proc.—IUPAC, Symp. Photochem. 10th*, **1984**, 257-258.
(4) A full account on the photocycloadditions with 1 will be published soon.
(5) Bryce-Smith, D.; Dadson, W. M.; Gilbert, A.; Orger, B. H.; Tyrrell, H. M. *Tetrahedron Lett.* **1978**, 1093.
(6) Still, I. W. J.; Leong, T. S. *Tetrahedron Lett.* **1979**, 1097.
(7) Osselton, E. M.; Lempers, E. L. M.; Cornelisse, J. *Proc.—IUPAC Symp. Photochem., 10th* **1984**, 161-162.
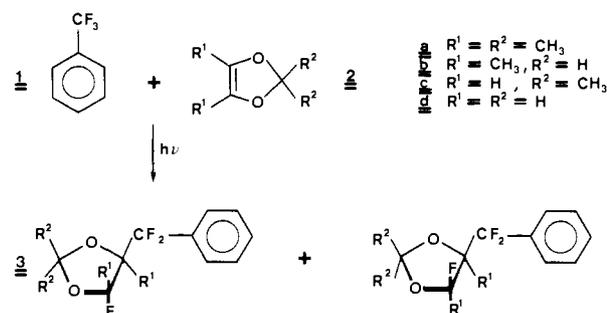
Table I. Free Enthalpies of Electron Transfer and Mode of Photoreactions of α,α,α-Trifluorotoluene (1) with Various Olefins

olefin	$E_{1/2}$,[a] V	ΔG,[b] eV	reaction mode[c] substitution	reaction mode[c] cycloaddition
2a	+0.42	−0.23	+	−
2b	+0.48	−0.17	+	−
2c	+0.69	+0.04	+	−
2d	+0.76	+0.11	+	ortho, meta
6a	+1.47	+0.82	−	meta
5	+1.83	+1.18	−	meta
6b[d]	−2.64	+1.72	−	meta

[a] Oxidation (reduction) potentials (vs. $Ag/AgNO_3$ electrode) were measured by cyclic voltametry (Pt working electrode) in acetonitrile: c(olefin) 1 mmol L^{-1}, c($LiClO_4$) 0.1 mol L^{-1}. [b] In dioxane with $E_{1/2}^{Red}(1)$ = −3.18 V or $E_{1/2}^{Ox}(1)$ = 2.91 V (consider also note d), ΔE_{excit} = 4.65 eV. [c] (−) + means (no) reaction; ortho (meta) means formation of ortho (meta)cycloadducts. [d] Here 1 acts as the donor and 7 as the acceptor (see text).

be rationalized on the basis of the thermodynamics of electron transfer.

Preparative irradiation (λ = 254 nm) of 2:1 mixtures in dioxane of 1 and of the olefins 2 and 6 respectively (concentration of 1: 0.1–0.5 mol L^{-1}) results in formation of products 3, 4, and mixtures of ortho, meta, and para cycloadducts 7–9[3,4]) in 60–80% yields

X = CH_2, C=O
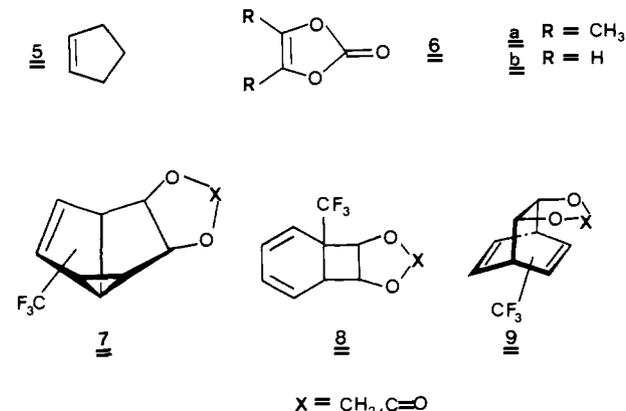
All products were separated by HPLC[8] and were identified by ^{1}H and ^{13}C NMR. Cornelisse and Osselton have found the same results in an independent study of the photoreaction of 1 with 6b.[9] In general substitution to 3 and 4 is only observed in photoreactions with the 1,3-dioxoles 2. Whereas 2a–c only yield the above mentioned products, the weaker donor olefin 2d already undergoes cycloaddition as the main reaction (90%). This obvious trend is continued in the photoreactions of 5[7] and 6, which exclusively proceed under cycloaddition onto the arene 1.[3,4] If it is assumed that the cycloaddition proceeds through a singlet exciplex[2,10,11]

(8) Chromosorb Si60 column, ethyl acetate–hexane mixture (3–50% ethyl acetate) as eluate.
(9) Cornelisse, J.; Osselton, E. M., University of Leiden, Netherlands, private communication.
(10) Mattay, J.; Runsink, J.; Leismann, H.; Scharf, H.-D. *Tetrahedron Lett.* **1982**, 4919.