tron rule.[14] The gas-phase results lead one to expect the synthesis of new stable dianions of formulas $Fe_2(CO)_6^{2-}$, $Cr_2(CO)_8^{2-}$, and $Cr_2(CO)_6^{2-}$.

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Registry No. Tetraethyllead, 78-00-2; nickel tetracarbonyl, 13463-39-3; iron pentacarbonyl, 13463-40-6; chromium hexacarbonyl, 13007-92-6.

[14] C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972).

Contribution from the Facolta Chimica Industriale,
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Sulfur-Sulfur Bond Cleavage Promoted by Palladium(0) and Platinum(0) Triphenylphosphine Complexes

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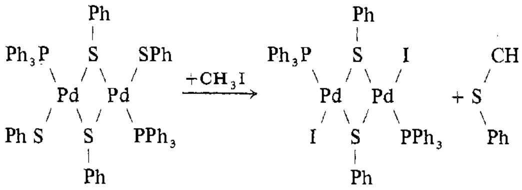
One of the more common features of transition metal complexes containing the coordinated SR^- group is their tendency to form polymeric units.[1] This tendency is greatly reduced as the electron-withdrawing properties of R increase. Thus, for $R = C_6F_5$ only monomeric species have been isolated.[2] However, generally the occurrence of monomers depends on the metal and also on the coordinated ligands, as shown in the cleavage of sulfur-sulfur bonds by $[Ni(L_\pi)_4]$ ($L_\pi = P(OR)_3$, CO), where both monomeric and polymeric derivatives are obtained.[3,4]

With the aim of verifying whether this behavior is common to zerovalent platinum triad metal complexes, we have examined the reaction of organic disulfides with complexes of the type $[M(PPh_3)_4]$ (M = Pt, Pd).

Results and Discussion

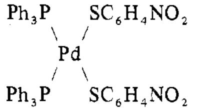
Oxidative addition of organic disulfides RSSR [$R = C_6H_5$, *o*- and *m*-$O_2NC_6H_4$, *t*-Bu, CN] to complexes of the type $[M(PPh_3)_4]$ (M = Pd, Pt) gives a variety of new compounds, the nature of which depends on both the reacting metal and the disulfide.

Reactions with $[Pd(PPh_3)_4]$. $[Pd(PPh_3)_4]$ reacts in benzene solution with $C_6H_5S\text{-}SC_6H_5$ under nitrogen to give a red compound formulated as a dimer having both terminal and bridging sulfide groups (I). This structure has been inferred on the basis of molecular weight measurements (mol wt in C_6H_6: calcd, 1174; found, 1130), elemental analysis, and reactivity with CH_3I to give II. $PhSCH_3$ was detected by glc using a Chromosorb column. Its formation probably occurs *via* an electrophilic attack of the positive end of $H_3C^+\cdots I^-$ on the sulfur atom of the terminal $-SC_6H_5$ group. Nucleophilic substitution of SR^- by I^- can be ruled out since no reaction occurs between I and iodide ion.



I II

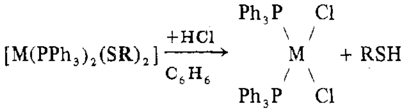
Monomeric compounds of type III are obtained in the reaction of $[Pd(PPh_3)_4]$ with electronegatively substituted aryl disulfides such as *o*- or *m*-nitrophenyl disulfide.



III

Reactions with $[Pt(PPh_3)_4]$. By treatment of $[Pt(PPh_3)_4]$ with electronegatively substituted or unsubstituted aryl disulfide only monomeric complexes are readily obtained. This accords with the smaller tendency of platinum relative to palladium to form polymeric units and with a decreased stability of such species owing to lower electron density on the sulfur atom in the electronegatively substituted aryl groups.

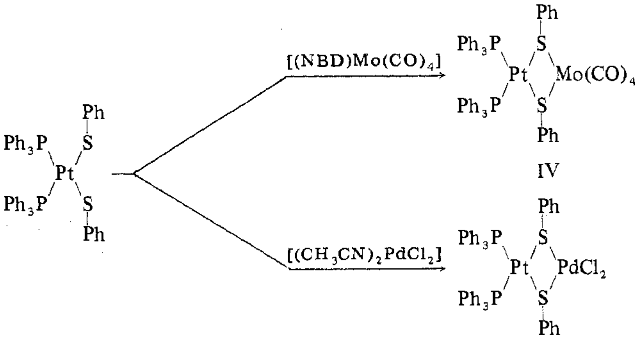
The complexes $[M(PPh_3)_2(SR)_2]$ (M = Pd, Pt), characterized by molecular weight measurements and by elemental analysis, react with hydrogen chloride according to the equation



$$[M(PPh_3)_2(SR)_2] \xrightarrow[C_6H_6]{+HCl} [M(PPh_3)_2Cl_2] + RSH$$

(M = Pd, $R = C_6H_4NO_2$, trans isomer ν(Pd-Cl) 360 cm^{-1}, Nujol mull; M = Pt, $R = C_6H_5$ and $C_6H_4NO_2$, cis isomer ν(Pt-Cl) 330 and 293 cm^{-1}, Nujol mull). The four-coordinate planar complexes $[M(PPh_3)_2Cl_2]$ were identified by comparison with authentic samples.[5,6]

The complex $[Pt(PPh_3)_2(SPh)_2]$ reacts also with transition metal compounds having labile groups such as norbornadiene or CH_3CN to give hetero dinuclear complexes according to



IV V

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[1] P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Amer. Chem. Soc.*, 87, 5251 (1965).

[2] R. S. Nyholm, J. F. Skiier, and M. H. Stiddard, *J. Chem. Soc. A*, 38 (1968).

[3] R. G. Hayter and F. S. Humiec, *J. Inorg. Nucl. Chem.*, 26, 807 (1964).

[4] H. Schott and G. Wilke, *Angew. Chem.*, 81, 896 (1969).

[5] G. Booth, *Advan. Inorg. Chem. Radiochem.*, 6, 1 (1964).

[6] D. M. Adams and P. J. Chandler, *J. Chem. Soc. A*, 588 (1969).

The ir spectrum of compound IV shows the expected bands for a cis-disubstituted octahedral metal carbonyl. A metal-metal bonding interaction Mo→Ti has been proposed by comparison of the ir spectra for the complexes $[PhS(CH_2)_2SPhMo(CO)_4]$ and $[(\pi\text{-}C_5H_5)_2Ti(SPh)_2Mo(CO)_4]$[7] (Table I). On the basis of the observed ir spectra a metal-metal interaction Mo→Pt can be ruled out.[8]

$[(Ph_3P)_2Pt(SPh)_2PdCl_2]$ is readily formed in benzene solution. Its ir spectrum contains a strong absorption band at 318 cm^{-1} attributable to ν(Pd-Cl), as confirmed by the ir spectrum of the corresponding iodo derivative obtained by metathesis.

Reaction with *tert*-Butyl Disulfide. In oxygen-free benzene $[M(PPh_3)_4]$ complexes (M = Pt, Pd) slowly react with *tert*-butyl disulfide to yield an air-sensitive product which analyzes as $[M(PPh_3)_2SC(CH_3)_3]_2$ and which was too unstable to permit a complete characterization.

Reactions with $(SCN)_2$. Thiocyanogen readily reacts in benzene with $[M(PPh_3)_4]$ to give N-bonded complexes[9-11] of the type *cis*-$[M(PPh_3)_2(NCS)_2]$ [M = Pt, ν(CN) 2080 cm^{-1}, ν(CS) 860 cm^{-1}; M = Pd, ν(CN) 2090 cm^{-1}, ν(CS) 845 cm^{-1}]. The ir data agree with those reported for the analogous $[M(PEt_3)_2(NCS)_2]$.[10]

Experimental Section

The complexes $[Pt(PPh_3)_4]$ and $[Pd(PPh_3)_4]$ were synthesized as reported in literature.[12,13] Benzene was distilled over sodium-potassium alloy and stored under nitrogen. All the other chemicals were reagent grade and used without further purification.

Infrared spectra in the region 4000-200 cm^{-1} were recorded using a Perkin-Elmer 457 spectrophotometer. Molecular weight measurements were carried out with a Mechrolab apparatus thermostated at 37°. Glc determinations were made with a Hewlett-Packard 5250 gas chromatograph using the appropriate columns.

Preparation of Complexes. Analytical data and melting points of the synthesized complexes are reported in Table II.

$[Pt(PPh_3)_2(SPh)_2]$. Equimolar amounts of $[Pt(PPh_3)_4]$ and PhSSPh were kept overnight at room temperature in benzene. The resulting yellow solution was concentrated at reduced pressure, and after addition of a 1:1 mixture of ethyl ether and petroleum ether, a yellow solid was obtained. It was collected by filtration, washed with the same mixture of solvents, and dried under vacuum; yield 85%.

The same procedure was used to prepare $[Pt(PPh_3)_2(o\text{-}O_2NC_6H_4S)_2]$ [yield 85%; infrared spectrum (Nujol mull): $\nu(NO_2)$ 1502, 1332 cm^{-1}] and $[Pt(PPh_3)_2(m\text{-}O_2NC_6H_4S)_2]$ [yield 80%; infrared spectrum (Nujol mull): $\nu(NO_2)$ 1517, 1343 cm^{-1}; mol wt in C_6H_6: calcd, 1027; found, 985].

$[Pt(PPh_3)_2(NCS)_2]$. To a benzene solution of $[Pt(PPh_3)_4]$ (1 m*M*) was added a solution (1 m*M*) of $(SNC)_2$, obtained as reported in literature,[14] in the same solvent, and the resulting mixture was allowed to react for 24 hr at room temperature. During this time a yellow solid began to form and the precipitation was completed by addition of ether. The resulting complex was washed with ether and dried under vacuum; yield 75%. Infrared spectrum (Nujol mull): ν(CN) 2080 cm^{-1}, ν(CS) 860 cm^{-1}.

$[Pt(PPh_3)_2(SPh)_2Mo(CO)_4]$. Equimolar amounts of $[Pt(PPh_3)_2(SPh)_2]$ and (norbornadiene)$Mo(CO)_4$[15] reacted in benzene overnight. The solution was concentrated and a yellow-brown solid was obtained

Table I. Carbonyl Stretching Frequencies of $[(Ph_3P)_2Pt(SPh)_2Mo(CO)_4]$ and Related Compounds

Compd	ν(CO), cm^{-1}	Solvent
$(Ph_3P)_2Pt(SPh)_2Mo(CO)_4$	2008, 1945, 1899, 1833	CH_2Cl_2
$(\pi\text{-}C_5H_5)_2Ti(SPh)_2Mo(CO)_4$[a]	2018, 1930, 1912, 1899	$CHCl_3$
$PhS(CH_2)_2SPhMo(CO)_4$[a]	2027, 1905 b, 1870	$CHCl_3$

[a] See ref 7.

Table II

Compd	Color	Mp, °C	% C		% H		% P		% S		% N		% halide	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[Pt(P(C_6H_5)_3)_2(C_6H_5S)_2]$	Yellow	193	61.45	61.8	4.29	4.3	6.60	6.31	6.83	6.8				
$[Pt(P(C_6H_5)_3)_2(m\text{-}NO_2C_6H_4S)_2]$	Red-orange	229	56.08	56.5	3.70	3.7			6.23	6.1	2.72	2.9		
$[Pt(P(C_6H_5)_3)_2(o\text{-}NO_2C_6H_4S)_2]$	Orange	142	56.08	56.7	3.70	3.8			6.23	6.1	2.72	2.8		
$[Pt(P(C_6H_5)_3)_2(NCS)_2]$	Pale yellow	233	54.47	54.1	3.62	3.6			7.67	7.7	3.35	3.25		
$[Pt(P(C_6H_5)_3)_2(C_6H_5S)_2Mo(CO)_4]$	Brown-yellow	152	54.49	54.2	3.50	3.5			5.60	5.6				
$[Pt(P(C_6H_5)_3)_2(C_6H_5S)_2PdCl_2]$	Yellow	253	51.60	51.7	3.62	3.6			5.76	5.8			6.36	6.3
$[PdP(C_6H_5)_3(C_6H_5S)_2]_2$	Red	168	61.35	61.7	4.29	4.3			10.92	11.0				
$[Pd(P(C_6H_5)_3)_2(m\text{-}NO_2C_6H_4S)_2]$	Red-orange	176	61.30	61.8	4.04	4.0	6.60	6.7	6.81	6.9	2.98	3.05		
$[Pd(P(C_6H_5)_3)_2(o\text{-}NO_2C_6H_4S)_2]$	Red-orange	113	61.30	61.8	4.04	4.1			6.81	6.6	2.98	3.05		
$[Pd(P(C_6H_5)_3)_2(NCS)_2]$	Red-orange	185	61.09	60.4	4.05	4.0			8.58	8.8	3.75	3.80		
$[PdP(C_6H_5)_3(C_6H_5S)I]_2$	Red	247	47.68	48.35	3.3	3.5			5.30	5.5			20.99	21.2

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(7) P. S. Braterman, V. A. Wilson, and K. K. Joshi, *J. Chem. Soc. A*, 191 (1971).

(8) P. S. Braterman, V. A. Wilson, and K. K. Joshi, *J. Organometal. Chem.*, 31, 123 (1971).

(9) (a) P. C. H. Mitchell and R. P. J. Williams, *J. Chem. Soc.*, 1912 (1960); (b) J. Lewis, R. S. Nyholm, and P. W. Smith, *ibid.*, 4590 (1961).

(10) (a) M. Chamberlain and J. C. Bailar, *J. Amer. Chem. Soc.*, 82, 1921 (1960); (b) A. Turco, and C. Pecile, *Nature (London)*, 191, 66 (1961); (c) M. E. Farago and J. M. James, *Inorg. Chem.*, 4, 962 (1965).

(11) J. Chatt and L. Ducanson, *Nature (London)*, **178**, 997 (1956).

(12) F. R. Hartley, *Organometal. Chem. Rev., Sect. A*, **6**, 122 (1970).

(13) L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).

(14) J. L. Wood, *Org. React.*, 3, 255 (1949).

(15) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

by addition of a 1:1 mixture of petroleum ether and ethyl ether; yield 75%. The infrared spectrum is reported in Table I.

$[Pt(PPh_3)_2(SPh)_2PdCl_2]$. Equimolar amounts of $[Pt(PPh_3)_2(SPh)_2]$ and $(CH_3CN)_2PdCl_2$ reacted in benzene for 6 hr. Concentration of the solution at reduced pressure and addition of ethyl ether to the resulting solution gave a yellow solid; yield 80%. Infrared spectrum (Nujol mull): ν(Pd–Cl) 318 (s), 330 (sh), 324 (sh), 306 (sh), 295 cm^{-1}. Mol wt in $CHCl_3$: calcd, 1115; found, 1036.

Palladium Complexes. All the complexes were prepared by the same procedures as those used for the analogous platinum derivatives: $[Pd(PPh_3)(SPh)_2]_2$: yield 85%; reaction time 10 hr. Mol wt in C_6H_6: calcd, 1174; found, 1130. $[Pd(PPh_3)_2(o\text{-}O_2NC_6H_4S)_2]$: yield 80%; reaction time 2 hr. Infrared spectrum (Nujol mull): $\nu(NO_2)$ 1502, 1326 cm^{-1}. Mol wt in C_6H_6: calcd, 939; found, 890. $[Pd(PPh_3)_2(m\text{-}O_2NC_6H_4S)_2]$: yield 70%; reaction time 2 hr. Infrared spectrum (Nujol mull): $\nu(NO_2)$ 1518, 1345 cm^{-1}. Mol wt in C_6H_6: calcd, 939; found, 915. $[Pd(PPh_3)_2(NCS)_2]$: yield 70%; reaction time 4 hr. Infrared spectrum (Nujol mull): ν(CN) 2090 cm^{-1}, ν(CS) 845 cm^{-1}.

$[Pd(PPh_3)(SPh)I]_2$. A benzene solution of $[Pd(PPh_3)(SPh)_2]_2$ reacted with an excess of CH_3I for 12 hr at room temperature. The resulting solution was concentrated at reduced pressure and addition of a 1:1 mixture of ethyl ether and petroleum ether produced a red solid, which was collected on a filter, washed with the same solvent, and dried under vacuum; yield 80%. In the mother liquor, analyzed by glc using a Chromosorb column, was detected $PhSCH_3$.

Reactions with HCl. In a typical experiment a benzene solution of $[Pt(PPh_3)_2(SPh)_2]$ reacted with hydrogen chloride for a few minutes. *cis*-$[Pt(PPh_3)_2Cl_2]$ was formed. Glc analysis of the solution on a Chromosorb column showed the presence of PhSH.

Acknowledgment. We thank Professor U. Belluco for his interest in this work. M. G. acknowledges C.N.R. (Rome) for partial financial support.

Registry No. $[Pt(PPh_3)_2(PhS)_2]$, 31168-85-1; $[Pt(PPh_3)_2(m\text{-}NO_2C_6H_4S)_2]$, 41507-74-8; $[Pt(PPh_3)_2(o\text{-}NO_2C_6H_4S)_2]$, 41507-75-9; $[Pt(PPh_3)_2(NCS)_2]$, 41507-76-0; $[Pt(PPh_3)_2(PhS)_2Mo(CO)_4]$, 41499-76-7; $[Pt(PPh_3)_2(PhS)_2PdCl_2]$, 41507-77-1; $[Pd(PPh_3)(PhS)_2]_2$, 41507-78-2; $[Pd(PPh_3)_2(m\text{-}NO_2C_6H_4S)_2]$, 41507-79-3; $[Pd(PPh_3)_2(o\text{-}NO_2C_6H_4S)_2]$, 41507-80-6; $[Pd(PPh_3)_2(NCS)_2]$, 41507-81-7; $[Pd(PPh_3)(PhS)I]_2$, 41507-82-8; $[Pt(PPh_3)_4]$, 14221-02-4; PhSSPh, 882-33-7; $(SNC)_2$, 505-14-6; (norbornadiene)$Mo(CO)_4$, 12146-37-1; $(CH_3CN)_2PdCl_2$, 14592-56-4; CH_3I, 74-88-4; $[Pd(PPh_3)_4]$, 14221-01-3; HCl, 7647-01-0.

Contribution from the Inorganic Materials Research Division,
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Dioxygenyl Salts $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$ and Their Convenient Laboratory Syntheses

D. E. McKee and Neil Bartlett*

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The first claim for the salt of formulation $O_2^+SbF_6^-$ was that of Young, *et al.*[1] These authors prepared their material by interaction of O_2F_2 with SbF_5. A puzzling feature of this report, however, was the rather large cubic unit cell quoted, for which *a* = 10.71 Å, since in the previously characterized[2] platinum analog *a* = 10.032 Å. In later papers Shamir and Binenboym described[3] a photochemical synthesis for what was claimed to be $O_2^+SbF_6^-$ and Beal, *et al.*, described[4] a preparation from SbF_5, F_2, and O_2 which simply involved heating this mixture. The first authors presented no unambiguous evidence for the formulation $O_2^+SbF_6^-$ and quoted a cubic unit cell constant of 10.30 Å, a value which, although more acceptable than that of Young, *et al.*, still seemed rather high. Beal, *et al.*, provided X-ray powder data to support a unit cell of 10.13 Å, a value in much closer harmony with the cell parameter for the cubic $O_2^+PtF_6^-$ salt.[2] The X-ray powder data of Beal, *et al.*, were, however, ascribed to a face-centered cell, whereas the full data (some of which was omitted from their tabulation) supported a body-centered cell with *a* = 10.13 Å. It is now clear that weak diffraction lines were omitted from their data. These represent (as discussed[2] by Bartlett and Lohmann for the $O_2^+PtF_6^-$ case) diffraction by the light atom superlattice and are of crucial structural importance.

In their differential thermal analysis of $O_2^+SbF_6^-$ Nikitina and Rosolovskii recognized[5] the existence of the $O_2^+Sb_2F_{11}^-$ salt as well as $O_2^+SbF_6^-$ and attempted a characterization of the two salts on the basis of X-ray powder data. Their data, however, are not that for the pure components $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$. Furthermore, Nikitina and Rosolovskii also failed to recognize $O_2^+SbF_6^-$ as an isomorph of $O_2^+PtF_6^-$.

Although the O_2^+ stretching frequency has been reported[6] for what was stated to be the $O_2^+SbF_6^-$ salt, the anion spectra were not given.

The X-ray powder data given in Table I and the Raman spectrum shown in Figure 1B characterize the $O_2^+SbF_6^-$ salt. The X-ray data establish that the compound is isomorphous with $O_2^+PtF_6^-$. The unit cell is cubic with $a = 10.132 \pm 0.002$ Å, $V = 1040$ Å^3, $Z = 8$, $d_c = 3.418$ g cm^{-3}. Since all observed reflections obey the conditions $h + k + l = 2n$ and $0kl$ where $k(l) = 2n$, the indicated space group is $Ia3$ (No. 206)[7] as established for O_2PtF_6.[2,8] The formula unit volume of 130 Å^3 is 2.4 Å^3 less than that found for $NO^+SbF_6^-$ by Bartlett and Jha.[9] This is comparable to the PtF_6^- case where[10] $V(NO^+PtF_6^-) = 129.5$ Å^3 and $V(O_2^+PtF_6^-) = 126.3$ Å^3. The close similarity of the intensities of the weak powder diffraction lines (oxygen and fluorine diffraction only), compared with those in the platinum relative,[9] suggests an isostructural relationship. Comparison of the Raman spectrum with that of $O_2^+PtF_6^-$ (given in Figure 1C) further supports the close structural similarity.

The X-ray powder data for $O_2^+Sb_2F_{11}^-$ given in Table II have not been indexed and all attempts to grow single crystals have failed. The Raman spectrum given in Figure 1A again gives clear evidence of the O_2^+ ion (in the band at 1865 cm^{-1}) and the anion spectrum shows relationship to the SbF_6^- spectrum. The anion spectrum is in fact simpler than in $XeF^+Sb_2F_{11}^-$ (ref 11) and $XeF_3^+Sb_2F_{11}^-$ (ref 12).

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[1] A. R. Young, II, T. Hirata, and S. I. Morrow, *J. Amer. Chem. Soc.*, 86, 20 (1964).

[2] N. Bartlett and D. H. Lohmann, *Proc. Chem. Soc., London*, 115 (1962).

[3] J. Shamir and J. Binenboym, *Inorg. Chim. Acta*, 2, 37 (1968).

[4] J. B. Beal, Jr., C. Pupp, and W. E. White, *Inorg. Chem.*, 8, 828 (1969).

[5] Z. K. Nikitina and V. Ya. Rosolovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2173 (1970).

[6] J. Shamir, J. Binenboym, and H. H. Claassen, *J. Amer. Chem. Soc.*, 90, 6223 (1968).

[7] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952.

[8] J. A. Ibers and W. C. Hamilton, *J. Chem. Phys.*, 44, 1748 (1966).

[9] N. Bartlett and D. H. Lohmann, *J. Chem. Soc.*, 619 (1964).

[10] N. Bartlett and S. P. Beaton, *Chem. Commun.*, 167 (1966).