by sublimation, giving colorless crystals having a melting point of 67 °C.

**Te[N(SiMe$_3$)$_2$]$_2$ (2).** The procedure for the preparation of **2** was identical with that of **1** except freshly sublimed $TeCl_4$ was first dissolved in toluene before being added to an $LiN(SiMe_3)_2$/*n*-hexane solution at −78 °C. In a typical preparation using 1.10 g of $LiN(SiMe_3)_2$ (6.57 mmol) and 0.51 g of $TeCl_4$ (1.89 mmol), a total of 0.43 g (0.97 mmol, 50% yield) of orange crystalline material having a melting point of 63–65 °C could be isolated by sublimation from the crude product. However, in order to obtain analytically pure product, the orange crystalline material had to be sublimed again twice (mp 69–71 °C). Anal. Found (calc for $H_{36}C_{12}N_2Si_4Te$): H, 8.17 (8.09); C, 32.48 (32.15); N, 6.28 (6.25). $^1$H NMR (ppm): 0.24. Mass spectrum (EI) [$m/z$ ($^{130}$Te peaks, %)]: 450 ($M^+$, 50), 289 ($M^+ - HN(SiMe_3)_2$, 20), 275 ($M^+ - TeMe_2 - Me$, 100).

For analysis of the volatile components from the preparation of **2**, 2.56 g of $LiN(SiMe_3)_2$ (15.3 mmol) and 1.03 g of $TeCl_4$ (3.81 mmol) were each added to separate arms of an H-shaped greaseless reaction vessel. After $LiN(SiMe_3)_2$ and $TeCl_4$ had each been dissolved in *n*-hexane (20 mL) and toluene (20 mL), respectively, the latter solution was decanted in small portions into the former at dry ice/acetone temperature. When the reaction was completed, the volatile components of the reaction mixture (at room temperature) were condensed into the empty ice/water-cooled arm of the vessel. The presence of $HN(SiMe_3)_2$ and absence of $SiMe_3Cl$ in the volatile component were then identified by adding small amounts of them to a sample of the latter and recording their $^1$H NMR spectra. A peak intensity enhancement was interpreted as a presence of the compound in the volatile component whereas a new peak indicated the compound's absence.

**Crystal Growth and X-ray Measurements of 1 and 2.** Crystals of **1** were grown over a period of 2–3 days by slowly condensing the solvent off an *n*-hexane solution of **1**. Crystals of **2** were grown overnight on the colder walls of a dynamically vacuum-pumped (<0.1 Torr) glass tube whose lower end, containing **2**, was kept in warm water (30–40 °C).

Both structures were measured on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 71.069 pm). Data were collected at −120 °C with a profile-fitting method,[11] $2\theta$ = 8–55° (**1**) and 8–50° (**2**). The structures were solved by Patterson methods and refined by full-matrix least squares, with all non-hydrogen atoms anisotropic. All hydrogen atoms were found by difference Fourier synthesis and refined isotropically. A riding model was employed for the hydrogen atoms with an idealized bond length of 96 pm. A semiempirical absorption correction was applied in both cases. All calculations were performed with SHELX.[12]

**Acknowledgment.** We wish to thank the Leibniz-Programm der Deutschen Forschungsgemeinschaft and the Fonds der Chemischen Industrie for operating grants and the Alexander von Humboldt Foundation for the award of a fellowship to M.B.

**Supplementary Material Available:** Tables of bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters (5 pages); listings of observed and calculated structural factors (21 pages). Ordering information is given on any current masthead page. Further details of the X-ray structural investigation can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, under quotation of the deposit number (CSD-54633), the authors, and the publication.

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# Preparation and Structural Characterization of Two Isomers of Stoichiometry $Re_2Cl_5(PR_3)_3$, Where R = Me or Et

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*Received June 25, 1990*

The paramagnetic dirhenium compounds of stoichiometry $Re_2Cl_5(PMe_3)_3$ have been prepared from the reactions of $Re_2Cl_4(PMe_3)_4$ with $Cl_2$(g) or with $PhI{\cdot}Cl_2$. Two isomers have been isolated and their structures determined. In terms of a numbering system to be explained in the text, in one isomer, 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**), the two $PMe_3$ ligands that are coordinated to a Re atom are trans to one another, while in the other isomer, 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**), the phosphines are cis. Attempts to convert the 1,2,7-isomer to the 1,3,6-isomer have been unsuccessful. A third compound, 1,3,6-$Re_2Cl_5(PEt_3)_3$ (**3**) was isolated from the reaction between $Re_2Cl_4(PEt_3)_4$ and $Ph_4P_2$. Pertinent crystal data are as follows: for **1**, monoclinic space group $C2/c$, $a$ = 13.157 (2) Å, $b$ = 12.033 (2) Å, $c$ = 28.197 (4) Å, $\beta$ = 92.84 (1)°, $V$ = 4459 (1) Å$^3$, $Z$ = 8; for **2**, monoclinic space group $P2_1/c$, $a$ = 8.973 (2) Å, $b$ = 8.752 (1) Å, $c$ = 28.691 (7) Å, $\beta$ = 90.21 (2)°, $V$ = 2253 (1) Å$^3$, $Z$ = 4; for **3**, $a$ = 11.589 (5) Å, $b$ = 14.795 (4) Å, $c$ = 17.942 (6) Å, $\beta$ = 97.73 (3)°, $V$ = 3048 (3) Å$^3$, $Z$ = 4.

## Introduction

Oxidative addition of halogens, disulfides, and diselenides to multiple metal–metal bonds is an area that has been explored in detail in this laboratory.[1] For example, $Cl_2$(g) reacts readily with compounds of the type $M_2Cl_4(dppe)_2$ (M = Mo or W) to form the $M_2Cl_6(dppe)_2$ compounds. We carried out reactions of the triply bonded complex $Re_2Cl_4(PMe_3)_4$[2] with $Cl_2$(g) (or with the use of $PhI{\cdot}Cl_2$, a solid chlorine equivalent) in the hope of obtaining a compound of stoichiometry $Re_2Cl_6(PMe_3)_4$. This target molecule would be of interest with regard to a compound of similar stoichiometry, namely $Re_2Cl_6(dppe)_2$, which was reported several years ago by Walton and co-workers.[3] This compound is quite unusual in that there is no Re–Re bond and hence it would have been interesting to see if $Re_2Cl_6(PMe_3)_4$ could adopt a similar structure. However, we have found that the reaction between $Re_2Cl_4(PMe_3)_4$ and $Cl_2$(g) yields 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**) (an explanation of our numbering system will follow shortly). When the same reaction is carried out in the presence of $PMe_3$, we obtained a different isomer, namely 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**).

The numbering system that we are employing here to distinguish the two isomers is as follows. (1) Place the $Re_2$ unit within a cube of ligands and number the latter in a clockwise direction as shown below:

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(1) (a) Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; O'Connor, C. J. *Inorg. Chem.* **1987**, *26*, 4051. (b) Canich, J. A. M.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R. *Inorg. Chem.* **1988**, *27*, 804. (c) Cotton, F. A.; Dunbar, K. R. *Inorg. Chem.* **1987**, *26*, 1305.

(2) (a) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987. (b) Root, D. R.; Blevins, C. H.; Lichtenberger, D. L.; Sattelberger, A. P.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *103*, 953.

(3) Jaecker, J. A.; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1975**, 698.

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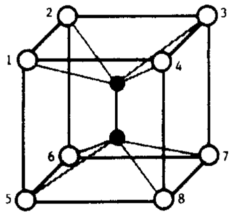

(2) Employ numbers (e.g., 1,3,6) to denote the positions of the substituent (i.e., phosphorus) atoms. (3) Use the numbers beginning with 1 that give the lowest total, for example, 1,3,6 rather than 1,3,8.

Although compounds of stoichiometry $Re_2X_5(PR_3)_3$ (X = Cl, Br; R = Et, Pr, $Me_2Ph$, $MePh_2$, $EtPh_2$) have been reported previously by Walton and co-workers,[4] no structural results were obtained. In this paper we report the crystal structures and some spectroscopic data for 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**), 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**), and also 1,3,6-$Re_2Cl_5(PEt_3)_3$ (**3**).

## Experimental Section

**Starting Materials.** General literature methods were used to prepare $Re_2Cl_4(PMe_3)_4$,[2] $Re_2Cl_4(PEt_3)_4$,[2a] and $PhI{\cdot}Cl_2$.[5] $Cl_2(g)$ was purchased from Matheson Gas Products, $PMe_3$ from Strem Chemicals, and $Ph_4P_2$ from Aldrich. Common solvents were obtained from commercial sources and distilled prior to use. All manipulations were carried out under an argon atmosphere by using standard vacuum-line techniques.

**Syntheses. (i) 1,3,6-$Re_2Cl_5(PMe_3)_3$ (1).** $Re_2Cl_4(PMe_3)_4$ (0.10 g, 0.12 mmol) was dissolved in 5 mL of dichloromethane. Approximately 4 mL (0.16 mmol) of $Cl_2(g)$ was syringed into the solution, which immediately turned dark blue-black in color. The mixture was stirred at room temperature for 12 h, after which the solvent was removed by vacuum distillation to leave a black residue. This was dissolved in 10 mL of dichloromethane and filtered to remove an insoluble white precipitate (probably $OPMe_3$). The filtrate was then concentrated to 5 mL, and then 10 mL of isomeric hexanes was added and the mixture placed in a refrigerator at −10 °C. After a few hours a black crystalline material, compound **1**, had precipitated out of solution. This was filtered off, washed with isomeric hexanes, and dried under vacuum; yield 0.081 g (88%). The reaction works equally well if $PhI{\cdot}Cl_2$ (0.034 g, 0.12 mmol) is used in place of $Cl_2(g)$.

**(ii) 1,2,7-$Re_2Cl_5(PMe_3)_3$ (2).** A solution containing $Re_2Cl_4(PMe_3)_4$ (0.10 g, 0.12 mmol), $PMe_3$ (15 μL, 0.15 mmol) and 5 mL of dichloromethane was stirred at room temperature for 5 min. No observable reaction or color change was observed. To this solution was added approximately 4 mL of $Cl_2(g)$ whereupon the solution gradually turned darker blue in color. The mixture was left to stir at room temperature for 12 h after which time the solvent was removed by vacuum distillation to leave a dark brown residue. This was redissolved in dichloromethane and filtered to remove a white precipitate of $OPMe_3$. The brown filtrate was placed in a Schlenk tube and carefully layered with isomeric hexanes. After a period of 5 weeks, large brown, block-shaped crystals of **2** grew on the walls and at the base of the tube. These were collected and washed with 5 mL of isomeric hexanes; yield 0.052 g (55%). The reaction works equally well if $PhI{\cdot}Cl_2$ (0.034 g, 0.12 mmol) is used in place of $Cl_2(g)$.

**(iii) 1,3,6-$Re_2Cl_5(PEt_3)_3$ (3).** A mixture of $Re_2Cl_4(PEt_3)_4$ (0.10 g, 0.10 mmol) and $Ph_4P_2$ (0.074 g, 0.20 mmol) was refluxed in 10 mL of benzene for 12 h. A green crystalline material, later found to be $Re_2Cl_6(PEt_3)_2$[2a,6] was filtered off. The red-brown filtrate was set aside and the solvent allowed to evaporate slowly. After several weeks, a very small amount of light green, platelike crystals of **3** had formed; yield ~5%.

**Preparation of Single Crystals.** Crystals of **1** and **2** suitable for X-ray analysis were grown by slow diffusion of isomeric hexanes into dichloromethane solutions at room temperature. Crystals of **3** were obtained as described above. All three sets of crystals were found to be stable in air.

**Physical Measurements.** Visible spectra were recorded on dichloromethane solutions in quartz cells (1 cm) on a Cary 17 UV-vis spectrometer. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($n$-$Bu_4NPF_6$ or TBAH) as the supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature. Under our experimental conditions, $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with the use of a Bioanalytical Systems Inc. Model 100 electrochemical analyzer. X-Band ESR spectra of dichloromethane solutions were recorded at 77 K with a frequency of 9.3 GHz on a Varian E-4 spectrometer interfaced to a MINC 11/23 Digital Systems computer.

**Table I.** Crystal Data for Compounds **1–3**

| | 1,3,6-$Re_2Cl_5(PMe_3)_3$ | 1,2,7-$Re_2Cl_5(PMe_3)_3$ | 1,3,6-$Re_2Cl_5(PEt_3)_3$ |
|---|---|---|---|
| formula | $Re_2Cl_5P_3C_9H_{27}$ | $Re_2Cl_5P_3C_9H_{27}$ | $Re_2Cl_5P_3C_{18}H_{45}$ |
| fw | 777.90 | 777.90 | 904.15 |
| space group | $C2/c$ (No. 15) | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) |
| $a$, Å | 13.157 (2) | 8.973 (2) | 11.589 (5) |
| $b$, Å | 12.033 (2) | 8.752 (1) | 14.795 (4) |
| $c$, Å | 28.197 (4) | 28.691 (7) | 17.942 (6) |
| $\beta$, deg | 92.84 (1) | 90.21 (2) | 97.73 (3) |
| $V$, Å$^3$ | 4459 (1) | 2253 (1) | 3048 (3) |
| $Z$ | 8 | 4 | 4 |
| $d_{calc}$, g/cm$^3$ | 2.318 | 2.293 | 1.970 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 118.091 | 116.841 | 86.504 |
| radiation monochromated in incident beam (λ, Å) | | Mo K$\alpha$ ($\lambda_\alpha$ = 0.71073 Å) | |
| temp, °C | 22 ± 1 | 22 ± 1 | 22 ± 1 |
| transm factors (max, min), % | 99.84, 62.06 | 99.84, 64.92 | 99.99, 39.27 |
| $R^a$ | 0.0353 | 0.0377 | 0.0728 |
| $R_w{}^b$ | 0.0489 | 0.0461 | 0.1047 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2\{|F_o|\}$.

**X-ray Structure Analysis.** Block-shaped crystals of **1** and **2** and a platelike crystal of **3** were glued to the tips of glass fibers with epoxy cement. For compounds **1** and **3**, a Nicolet P3/F Equivalent diffractometer was used while for **2** an Enraf-Nonius CAD-4F diffractometer was employed. Data collection, by procedures that have been described previously,[7] was carried out at room temperature. Details are summarized in Table I. The unit cell parameters and orientation matrices were refined by a least-squares fit to the positions of 25 reflections. The $\omega$–$2\theta$ scan technique was used to gather data points in the range $4 \leq 2\theta \leq 50°$ (45° in the case of **2**). Three check reflections monitored throughout data collection displayed no significant gain or loss in intensity. Data reduction was carried out by using well-established computational procedures.[8] The data were corrected for Lorentz and polarization effects and azimuthal scans of reflections having an Eulerian angle $\chi$ near 90° were used as a basis for an empirical absorption correction.[9]

For compounds **1** and **2**, the positions of the Re atoms were determined from the Patterson map. Following least-squares refinements on the metal atom parameters, a difference Fourier map revealed the atoms of the coordination sphere and some of the carbon atoms. Subsequent least-squares refinements and difference Fourier maps then revealed the remaining carbon atoms. Final least-squares refinements gave satisfactorily low discrepancy indices, as listed in Table I.

For compound **3**, a weak diffractor, the positions of four Re, five Cl and three P atoms were located by using the direct-methods program in SHELXS-86.[10] During least-squares refinement the site occupancy factors (sof's) of the two pairs of Re atoms (Re(1), Re(2) and Re(3), Re(4)) were allowed to vary but were constrained so that their sum equaled 1. The sof's settled to values of 0.666 and 0.333. After a succession of difference Fourier maps and least-squares cycles, all atoms were located in addition to a third pair of Re atoms (Re(5), Re(6)), i.e., a third orientation. These were also included in the refinement and their sof's allowed to vary against those of Re(1), Re(2) and Re(3), Re(4). The sof's converged to final values of 0.642 for Re(1), Re(2), 0.321 for Re(3), Re(4), and 0.037 for Re(5), Re(6). After isotropic convergence of all the non-hydrogen atoms, the absorption correction DIFABS[11] was applied.

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**Table II.** Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**)

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| Re(1) | 0.73066 (4) | 0.53362 (4) | 0.11431 (2) | 2.139 (9) |
| Re(2) | 0.86209 (3) | 0.42202 (4) | 0.13034 (2) | 2.030 (8) |
| Cl(1) | 0.5821 (3) | 0.4264 (3) | 0.1114 (2) | 4.08 (8) |
| Cl(2) | 0.7735 (3) | 0.7221 (3) | 0.1048 (1) | 3.47 (7) |
| Cl(3) | 0.9339 (3) | 0.3612 (3) | 0.0608 (1) | 3.37 (7) |
| Cl(4) | 0.7869 (3) | 0.2434 (3) | 0.1355 (1) | 3.76 (7) |
| Cl(5) | 0.8945 (3) | 0.4153 (3) | 0.2121 (1) | 3.43 (7) |
| P(1) | 0.6771 (3) | 0.5847 (3) | 0.1930 (1) | 3.31 (7) |
| P(2) | 0.7132 (3) | 0.5232 (3) | 0.0284 (1) | 3.16 (7) |
| P(3) | 0.9991 (3) | 0.5593 (3) | 0.1319 (1) | 2.63 (6) |
| C(1) | 0.559 (1) | 0.667 (1) | 0.1831 (7) | 5.2 (4) |
| C(2) | 0.635 (1) | 0.470 (2) | 0.2308 (6) | 5.3 (4) |
| C(3) | 0.758 (1) | 0.674 (1) | 0.2309 (6) | 4.8 (4) |
| C(4) | 0.812 (1) | 0.586 (1) | −0.0059 (5) | 4.2 (3) |
| C(5) | 0.685 (1) | 0.386 (1) | 0.0011 (5) | 5.1 (4) |
| C(6) | 0.600 (1) | 0.604 (1) | 0.0109 (6) | 4.9 (4) |
| C(7) | 1.115 (1) | 0.483 (1) | 0.1477 (6) | 4.3 (3) |
| C(8) | 1.026 (1) | 0.633 (1) | 0.0770 (5) | 3.4 (3) |
| C(9) | 1.004 (1) | 0.666 (1) | 0.1774 (5) | 3.9 (3) |

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**Table III.** Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**)

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| Re(1) | 0.22368 (3) | −0.01725 (3) | 0.12397 (1) | 1.657 (5) |
| Re(2) | 0.25257 (3) | 0.23205 (4) | 0.13650 (1) | 1.853 (6) |
| Cl(1) | 0.4671 (2) | −0.1207 (3) | 0.10963 (9) | 3.47 (5) |
| Cl(2) | 0.1783 (3) | −0.1034 (3) | 0.04658 (8) | 3.36 (4) |
| Cl(3) | 0.0305 (2) | 0.3682 (3) | 0.12674 (9) | 3.48 (4) |
| Cl(4) | 0.2296 (3) | 0.2883 (3) | 0.21689 (8) | 3.22 (4) |
| Cl(5) | 0.5074 (2) | 0.2636 (3) | 0.14441 (9) | 3.57 (5) |
| P(1) | −0.0430 (2) | −0.0256 (3) | 0.12950 (8) | 2.36 (4) |
| P(2) | 0.2744 (2) | −0.1046 (3) | 0.20156 (8) | 2.67 (4) |
| P(3) | 0.2967 (3) | 0.2980 (3) | 0.05528 (8) | 2.99 (5) |
| C(1) | −0.099 (1) | −0.227 (1) | 0.1312 (5) | 4.9 (3) |
| C(2) | −0.1489 (9) | 0.049 (1) | 0.0800 (3) | 3.5 (2) |
| C(3) | −0.135 (1) | 0.057 (1) | 0.1800 (4) | 3.9 (2) |
| C(4) | 0.149 (1) | −0.081 (1) | 0.2502 (4) | 4.2 (2) |
| C(5) | 0.455 (1) | −0.050 (1) | 0.2258 (4) | 4.4 (2) |
| C(6) | 0.283 (1) | −0.310 (1) | 0.1972 (4) | 4.8 (2) |
| C(7) | 0.443 (1) | 0.199 (1) | 0.0264 (4) | 4.4 (2) |
| C(8) | 0.138 (1) | 0.292 (1) | 0.0160 (4) | 5.2 (3) |
| C(9) | 0.347 (1) | 0.497 (1) | 0.0551 (4) | 5.1 (3) |

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Following this all atoms, except Re(5) and Re(6), were refined anisotropically to give residuals of $R = 0.0728$ and $R_w = 0.1047$. In the final difference map there were no peaks greater than 1 e Å$^{-3}$. The relatively high *R* values are presumably due to our inability to model the disorder precisely.

The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Tables II–IV list the positional parameters for compounds **1**–**3**, respectively. Selected bond distances and angles for **1**–**3** are found in Tables V–VII, respectively. Complete tables of crystal parameters, data collection, structure refinement, bond distances, and bond angles as well as anisotropic thermal parameters and tables of structure factors are available as supplementary material.

**Table IV.** Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for 1,3,6-$Re_2Cl_5(PEt_3)_3$ (**3**)

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| Re(1)[b] | 0.2456 (1) | 0.04693 (9) | 0.20354 (8) | 4.23 (3) |
| Re(2)[b] | 0.3480 (1) | 0.14940 (9) | 0.27474 (8) | 4.78 (4) |
| Re(3)[c] | 0.3641 (3) | 0.0894 (2) | 0.2029 (2) | 5.39 (8) |
| Re(4)[c] | 0.2187 (3) | 0.1045 (2) | 0.2700 (2) | 6.05 (9) |
| Re(5)[d] | 0.327 (3) | 0.047 (2) | 0.278 (2) | 7 (1)* |
| Re(6)[d] | 0.245 (4) | 0.164 (3) | 0.208 (3) | 10 (2)* |
| Cl(1) | 0.3700 (6) | −0.0734 (4) | 0.1790 (4) | 7.4 (2) |
| Cl(2) | 0.0499 (7) | 0.1067 (6) | 0.1820 (5) | 9.6 (2) |
| Cl(3) | 0.4410 (6) | 0.2420 (5) | 0.1960 (4) | 8.3 (2) |
| Cl(4) | 0.2128 (7) | 0.2629 (5) | 0.2851 (5) | 9.8 (3) |
| Cl(5) | 0.3232 (8) | 0.1116 (6) | 0.4001 (4) | 10.3 (3) |
| P(1) | 0.2618 (6) | 0.1073 (5) | 0.0767 (4) | 5.8 (2) |
| P(2) | 0.1627 (7) | −0.0531 (6) | 0.2906 (4) | 7.4 (2) |
| P(3) | 0.5399 (5) | 0.0806 (4) | 0.2978 (4) | 5.5 (2) |
| C(1) | 0.204 (3) | 0.223 (2) | 0.059 (2) | 10 (1) |
| C(2) | 0.114 (3) | 0.248 (2) | 0.002 (2) | 11 (1) |
| C(3) | 0.165 (2) | 0.032 (2) | 0.014 (2) | 10 (1) |
| C(4) | 0.194 (3) | −0.057 (2) | −0.004 (2) | 9 (1) |
| C(5) | 0.409 (2) | 0.090 (2) | 0.039 (2) | 9 (1) |
| C(6) | 0.399 (6) | 0.126 (4) | −0.034 (2) | 23 (3) |
| C(7) | 0.558 (2) | −0.024 (2) | 0.354 (1) | 7.5 (8) |
| C(8) | 0.664 (2) | −0.042 (2) | 0.399 (2) | 11 (1) |
| C(9) | 0.623 (3) | 0.055 (2) | 0.219 (2) | 12 (1) |
| C(10) | 0.733 (3) | 0.014 (5) | 0.233 (3) | 28 (3) |
| C(11) | 0.623 (4) | 0.172 (2) | 0.343 (2) | 13 (1) |
| C(12) | 0.632 (4) | 0.197 (3) | 0.419 (2) | 18 (2) |
| C(13) | 0.257 (2) | −0.133 (2) | 0.344 (1) | 8.1 (9) |
| C(14) | 0.207 (3) | −0.205 (2) | 0.379 (2) | 12 (1) |
| C(15) | 0.073 (3) | −0.129 (3) | 0.244 (2) | 16 (2) |
| C(16) | 0.086 (4) | −0.189 (3) | 0.186 (2) | 17 (2) |
| C(17) | 0.066 (3) | 0.023 (4) | 0.347 (2) | 19 (2) |
| C(18) | 0.011 (6) | −0.027 (5) | 0.399 (5) | 27 (4) |

[a] Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Site modeled as 0.642 Re. [c] Site modeled as 0.321 Re. [d] Site modeled as 0.037 Re.

**Table V.** Selected Bond Distances (Å) and Angles (deg) for 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**)[a]

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Re(1)–Re(2) | 2.218 (1) | Re(2)–Cl(3) | 2.336 (3) |
| Re(1)–Cl(1) | 2.340 (4) | Re(2)–Cl(4) | 2.373 (3) |
| Re(1)–Cl(2) | 2.356 (3) | Re(2)–Cl(5) | 2.324 (3) |
| Re(1)–P(1) | 2.440 (4) | Re(2)–P(3) | 2.444 (3) |
| Re(1)–P(2) | 2.425 (4) | P(1)–C(1) | 1.85 (2) |
| | Bond Angles | | |
| Re(2)–Re(1)–Cl(1) | 108.34 (9) | Re(1)–Re(2)–Cl(4) | 103.73 (9) |
| Re(2)–Re(1)–Cl(2) | 114.67 (9) | Re(1)–Re(2)–Cl(5) | 109.03 (9) |
| Re(2)–Re(1)–P(1) | 102.98 (9) | Re(1)–Re(2)–P(3) | 99.28 (8) |
| Re(2)–Re(1)–P(2) | 101.93 (9) | CL(3)–Re(2)–Cl(4) | 87.4 (1) |
| Cl(1)–Re(1)–Cl(2) | 137.0 (1) | Cl(3)–Re(2)–Cl(5) | 139.4 (1) |
| Cl(1)–Re(1)–P(1) | 83.8 (1) | Cl(3)–Re(2)–P(3) | 84.2 (1) |
| Cl(1)–Re(1)–P(2) | 84.2 (1) | Cl(4)–Re(2)–Cl(5) | 88.0 (1) |
| Cl(2)–Re(1)–P(1) | 86.7 (1) | Cl(4)–Re(2)–P(3) | 157.0 (1) |
| Cl(2)–Re(1)–P(2) | 87.0 (1) | Cl(5)–Re(2)–P(3) | 84.6 (1) |
| P(1)–Re(1)–P(2) | 154.7 (1) | Re(1)–P(1)–C(1) | 106.0 (6) |
| Re(1)–Re(2)–Cl(3) | 111.22 (8) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

## Discussion

**Preparation and Structural Characterization.** An oxidative substitution reaction between $Re_2Cl_4(PMe_3)_4$ and $Cl_2(g)$ occurs to give 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**) in high yield. An ORTEP diagram of the molecule, shown in Figure 1, clearly shows that the two phosphines that are coordinated to the same Re atom are trans to one another; i.e., the P(1)–Re(1)–P(2) angle is 154.7 (1)°. The Re–Re bond length of 2.218 (1) Å is indicative of a multiple bond. Since this molecule contains a $Re_2^{5+}$ core, the electronic configuration must be $\sigma^2\pi^4\delta^2\delta^{*1}$, giving rise to a bond order of 3.5.

When $Re_2Cl_4(PMe_3)_4$ is treated with $Cl_2(g)$, in the presence of $PMe_3$ which we added in the hope that Re–P bond cleavage would be thwarted, a compound of the same stoichiometry results, namely 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**). In this case two of the phosphines are cis to one another; i.e., the P(1)–Re(1)–P(2) angle is 96.60 (7) Å. An ORTEP diagram for **2** is shown in Figure 2. The

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(11) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

**Table VI.** Selected Bond Distances (Å) and Angles (deg) for 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**)[a]

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Re(1)–Re(2) | 2.226 (1) | Re(2)–Cl(3) | 2.338 (2) |
| Re(1)–Cl(1) | 2.401 (2) | Re(2)–Cl(4) | 2.368 (2) |
| Re(1)–Cl(2) | 2.379 (2) | Re(2)–Cl(5) | 2.314 (2) |
| Re(1)–P(1) | 2.400 (2) | Re(2)–P(3) | 2.435 (2) |
| Re(1)–P(2) | 2.396 (2) | P(1)–C(1) | 1.829 (10) |
| Bond Angles | | | |
| Re(2)–Re(1)–Cl(1) | 106.96 (6) | Re(1)–Re(2)–Cl(4) | 110.52 (6) |
| Re(2)–Re(1)–Cl(2) | 118.75 (6) | Re(1)–Re(2)–Cl(5) | 104.33 (6) |
| Re(2)–Re(1)–P(1) | 97.74 (5) | Re(1)–Re(2)–P(3) | 95.57 (6) |
| Re(2)–Re(1)–P(2) | 98.11 (5) | Cl(3)–Re(2)–Cl(4) | 86.18 (8) |
| Cl(1)–Re(1)–Cl(2) | 82.73 (8) | Cl(3)–Re(2)–Cl(5) | 142.43 (8) |
| Cl(1)–Re(1)–P(1) | 155.18 (8) | Cl(3)–Re(2)–P(3) | 84.61 (8) |
| Cl(1)–Re(1)–P(2) | 82.47 (8) | Cl(4)–Re(2)–Cl(5) | 88.23 (8) |
| Cl(2)–Re(1)–P(1) | 83.37 (8) | Cl(4)–Re(2)–P(3) | 153.90 (8) |
| Cl(2)–Re(1)–P(2) | 142.89 (8) | Cl(5)–Re(2)–P(3) | 84.34 (9) |
| P(1)–Re(1)–P(2) | 96.60 (7) | Re(1)–P(1)–C(1) | 107.7 (4) |
| Re(1)–Re(2)–Cl(3) | 112.43 (6) | | |

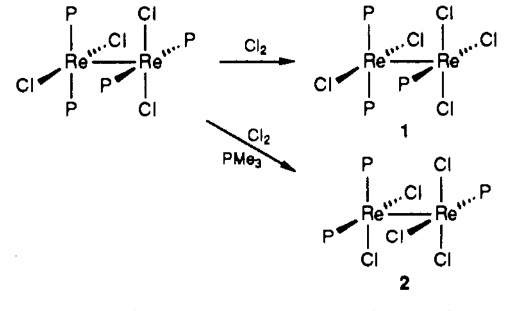
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

**Table VII.** Selected Bond Distances (Å) and Angles (deg) for 1,3,6-$Re_2Cl_5(PEt_3)_3$ (**3**)[a]

| | | | |
|---|---|---|---|
| Bond Distances | | | |
| Re(1)–Re(2) | 2.221 (2) | Re(2)–Cl(4) | 2.322 (9) |
| Re(1)–Cl(1) | 2.369 (7) | Re(2)–Cl(5) | 2.372 (8) |
| Re(1)–Cl(2) | 2.416 (8) | Re(2)–P(3) | 2.430 (6) |
| Re(1)–P(1) | 2.476 (7) | P(1)–C(1) | 1.85 (3) |
| Re(1)–P(2) | 2.441 (8) | Re(3)–Re(4) | 2.210 (5) |
| Re(2)–Cl(3) | 2.334 (8) | Re(5)–Re(6) | 2.27 (6) |
| Bond Angles | | | |
| Re(2)–Re(1)–Cl(1) | 109.2 (2) | Re(1)–Re(2)–Cl(4) | 103.0 (2) |
| Re(2)–Re(1)–Cl(2) | 105.1 (2) | Re(1)–Re(2)–Cl(5) | 105.1 (2) |
| Re(2)–Re(1)–P(1) | 100.5 (2) | Re(1)–Re(2)–P(3) | 102.6 (2) |
| Re(2)–Re(1)–P(2) | 105.8 (2) | Cl(3)–Re(2)–Cl(4) | 89.7 (3) |
| Cl(1)–Re(1)–Cl(2) | 145.8 (3) | Cl(3)–Re(2)–Cl(5) | 146.9 (3) |
| Cl(1)–Re(1)–P(1) | 88.7 (2) | Cl(3)–Re(2)–P(3) | 82.1 (2) |
| Cl(1)–Re(1)–P(2) | 88.0 (3) | Cl(4)–Re(2)–Cl(5) | 85.7 (3) |
| Cl(2)–Re(1)–P(1) | 84.6 (3) | Cl(4)–Re(2)–P(3) | 154.4 (3) |
| Cl(2)–Re(1)–P(2) | 83.2 (3) | Cl(5)–Re(2)–P(3) | 88.0 (3) |
| P(1)–Re(1)–P(2) | 153.2 (2) | Re(1)–P(1)–C(1) | 115 (1) |
| Re(1)–Re(2)–Cl(3) | 107.9 (2) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

formation of compound **2** involves not only oxidative ligand substitution but also ligand rearrangement at, at least, one metal center:



We are unsure of the exact mechanism for the formation of **2**, but since we were able to prepare it in no better than a 55% yield, we presume that the pathway must involve some decomposition. A significant amount of trimethylphosphine oxide ($OPMe_3$) was isolated along with some other byproducts that we were unable to characterize. Although the mechanism is obscure, the reaction is completely reproducible. The Re–Re bond distance in **2** is 2.226 (1) Å (i.e., essentially the same as that in **1**) and thus is consistent with a bond order of 3.5.

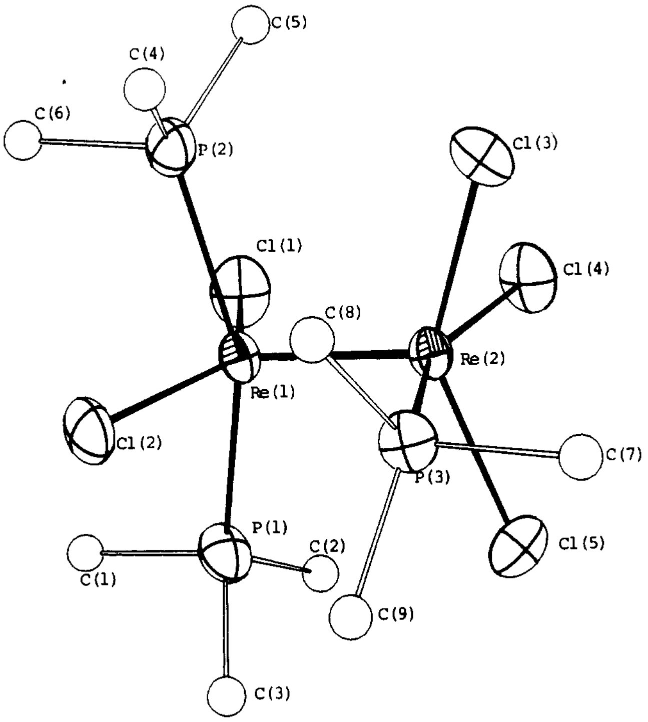


**Figure 1.** ORTEP diagram of 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**) showing 50% probability ellipsoids. Carbon atoms are shown as spheres of arbitrary radii.

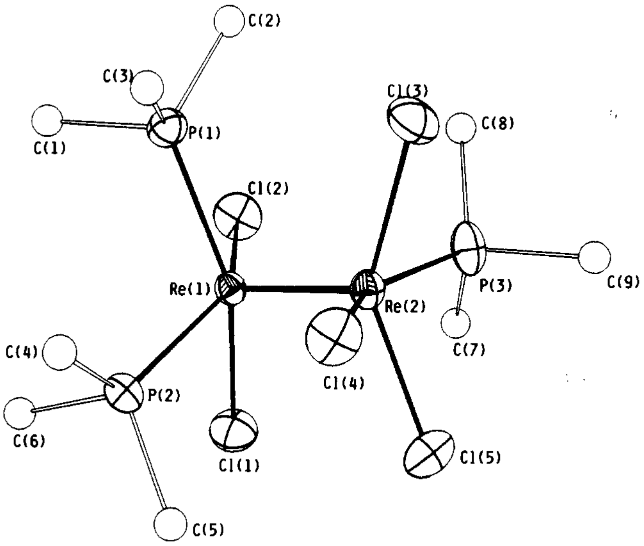


**Figure 2.** ORTEP diagram of 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**) showing 50% probability ellipsoids. Carbon atoms are shown as spheres of arbitrary radii.

We have included the structure of 1,3,6-$Re_2Cl_5(PEt_3)_3$ (**3**) for comparison. This compound is not new, having been reported by Walton several years ago.[4a] We isolated a few crystals of **3** from the reaction between $Re_2Cl_4(PEt_3)_4$[2a] and $Ph_4P_2$. Obviously, the $Ph_4P_2$ plays no part in the reaction and so we suspect either (a) that **3** was present in the $Re_2Cl_4(PEt_3)_4$ starting material or (b) that some decomposition of $Re_2Cl_4(PEt_3)_4$ occurred during the course of the reaction, liberating free $Cl^-$ ions which then reacted with $Re_2Cl_4(PEt_3)_4$ forming **3**. The Re–Re distance in this derivative is 2.221 (2) Å, and the P(1)–Re(1)–P(1) angle is 153.2 (2)°.

One interesting feature of this structure, illustrated in Figure 3, is that the $Re_2$ unit is disordered in three directions within the quasi-cube of Cl and P ligands. This type of crystallographic disorder has already been addressed in detail elsewhere.[6,12] The percentage occupancies for the three disordered $Re_2$ units are

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[12] Cotton, F. A.; Jennings, J. G.; Price, A. C.; Vidyasagar, K. *Inorg. Chem.* **1990**, *29*, 4138.

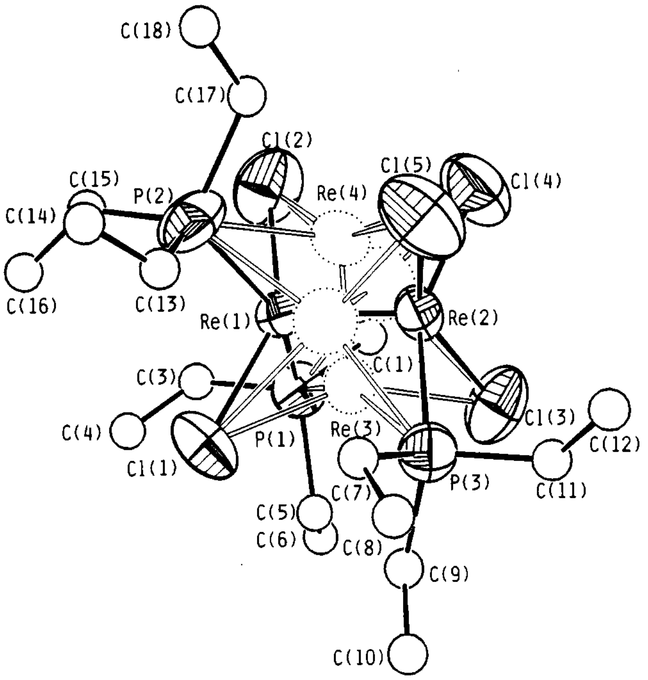

**Figure 3.** ORTEP diagram of 1,3,6-$Re_2Cl_5(PEt_3)_3$ (**3**) showing 50% probability ellipsoids. Carbon atoms are shown as spheres of arbitrary radii, and the minor orientations of two $Re_2$ units are shown as dashed lines.

**Table VIII.** Electrochemical and Spectroscopic Data for Compounds **1**–**3**

| complex | CV half-wave potentials, V[a] $E_{1/2}(1)$ | CV half-wave potentials, V[a] $E_{1/2}(2)$ | electronic abs spectral data: λ, nm (ε)[b] |
|---|---|---|---|
| 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**) | +0.46 (ox) | −0.75 (red) | 1314 (2300), 698 (40), 590 (100), 555 (sh), 468 (130), 3896 (sh), 355 (1700) |
| 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**) | +0.68 (ox) | −0.48 (red) | 1283 (2200), 760 (40), 570 (150), 468 (100), 372 (2320) |
| 1,3,6-$Re_2Cl_5(PEt_3)_3$ (**3**)[c] | +0.34 (ox) | −0.88 (red) | 1460, 720 |

[a] Measured on 0.1 M TBAH–$CH_2Cl_2$ solutions and referenced to the Ag/AgCl electrode. Scan rate $v$ = 200 mV/s at a Pt disk electrode. [b] Dichloromethane solutions. [c] Data taken from ref 4a,b.

64.2%, 32.1%, and 3.70%. It should be noted that for all three orientations, the molecule is always the 1,3,6-isomer.

**Electrochemical and Spectroscopic Properties.** Table VIII summarizes the electrochemical and visible spectral data for compounds **1**–**3**. All three display similar cyclic voltammograms, namely, a reversible oxidation at potentials ranging from +0.34 to +0.68 V (vs. the Ag/AgCl reference electrode) and a reversible reduction at −0.48 V to −0.88 V. These values are similar to those obtained for other derivatives.[4] These $Re_2^{5+}$ species exhibit strong, broad absorptions in the range 1280–1460 nm. This band is typical of species containing a $\sigma^2\pi^4\delta^2\delta^{*1}$ electronic configuration[2a,13] and may be assigned to a $\delta^2\delta^* \rightarrow \delta\delta^{*2}$ transition.

The X-band ESR spectra of dichloromethane glasses of **1** and **2** were recorded at −160 °C and confirm the paramagnetism of these complexes. The spectrum of **1** (that of **2** is very similar) is shown in Figure 4. A complex pattern is observed that shows a considerable amount of hyperfine coupling to the rhenium ($I = {}^5/_2$) and phosphorus ($I = {}^1/_2$) nuclei. The spectra are centered at ~3000 G giving a value of $g \sim 2.2$ for both complexes. The values of $g_\perp$ and $g_\parallel$ cannot be determined from these complex spectral patterns.

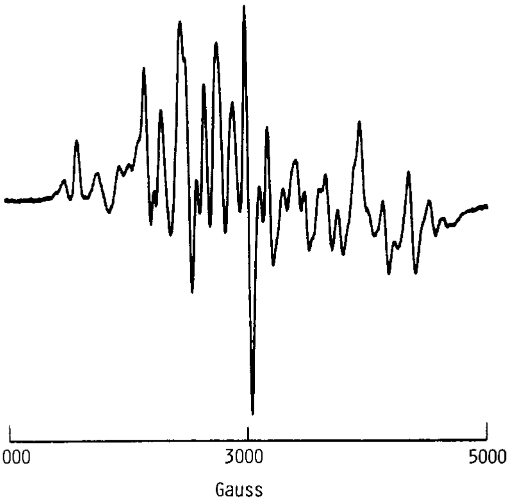

**Figure 4.** X-Band ESR spectrum, in a frozen dichloromethane solution at −160 °C, for 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**).

**Thermal Stability and Isomerization.** Compounds **1** and **2** are the only examples of two isomers in the $Re_2Cl_5(PR_3)_3$ class of compounds that have been structurally characterized to date. Walton[4c] has claimed to have isolated two isomers of $Re_2Cl_5(PMe_2Ph)_3$, but structural evidence is lacking. Compound **2** is the only derivative known of a dimetal complex that has two monodentate phosphines cis to one another. For compounds of the type $Re_2X_4(PR_3)_4$[12–14] (X = halide) the only isomer known is the 1,3,6,8-isomer; i.e., all the phosphines are trans to one another, and in the class $Re_2X_6(PR_3)_2$[6,15,16] the 1,7-isomer (all phosphines trans) is the only one that has been isolated. Hence, we suspected that **2** may be unstable relative to **1**. We made several attempts to convert **2** to **1** (and also **1** to **2**) by refluxing them in a variety of solvents for various periods of time and monitoring their progress by cyclic voltammetry. In chlorinated solvents, such as dichloromethane and chloroform, no conversion was observed, even after refluxing for 7 days. When we resorted to higher-boiling solvents such as 1,2-dichloroethane, THF, benzene, or toluene, the compounds appeared to decompose to mixtures of unidentifiable products. Thus, we must conclude from these studies that the activation barrier is too high ($E_a$ > 30 kcal $mol^{-1}$) to allow conversion to proceed smoothly at temperatures below about 60 °C, while at higher temperatures we observe the onset of processes leading to decomposition.

**Acknowledgment.** We thank the National Science Foundation for financial support and Dr. Phillip Hanna of the University of New Hampshire for assistance with the ESR spectral measurements.

**Supplementary Material Available:** For the crystal structures of **1**–**3**, full tables of crystal parameters and details of the data collection and refinement, bond distances, bond angles, and anisotropic displacement parameters (18 pages); tables of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

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(13) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Thomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

(14) (a) Cotton, F. A.; Frenz, B. A.; Ebner, J. R.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1974**, 4. (b) Cotton, F. A.; Frenz, B. A.; Walton, R. A.; *Inorg. Chem.* **1976**, *15*, 1630.

(15) (a) Bennett, M. J.; Cotton, F. A.; Foxman, B. M.; Stokely, P. F. *J. Am. Chem. Soc.* **1967**, *89*, 2759. (b) Cotton, F. A.; Foxman, B. M. *Inorg. Chem.* **1968**, *7*, 2135.

(16) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chim. Acta* **1988**, *144*, 17.