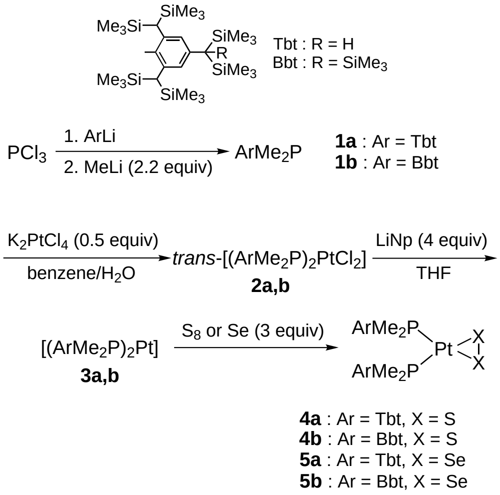
The First Disulfur and Diselenium Complexes of Platinum: Syntheses and Crystal Structures**

Kazuto Nagata, Nobuhiro Takeda, and
Norihiro Tokitoh*

Various kinds of transition metal compounds containing a polychalcogenido ligand have been synthesized and characterized.[1] In particular, the chemistry of complexes with diatomic chalcogen ligands has attracted much attention because of their unique structure,[2] biological interest,[3] potential for hydrogen-transfer catalysis,[2] and synthetic utility as a precursor of new metal cluster complexes.[4] However, since sulfur and selenium ligands have a strong propensity for bridging metal atoms, it is often difficult to prepare their mononuclear diatomic complexes.[2, 5] As for mononuclear platinum polychalcogenido compounds, most of the complexes obtained so far are limited to PtE_5 or PtE_4 (E = S, Se) ring systems, for example, $[(NH_4)_2Pt(S_5)_3]$,[6] $[(PPh_3)_2PtS_4]$,[7] and $[(dppe)PtSe_4]$ (dppe = 1,2-bis(diphenylphosphino)ethane).[8] To our knowledge, the disulfur and diselenium complexes of platinum remain unknown, although the dioxygen analogues, for example, $[(Ph_3P)_2PtO_2]$,[9] have been extensively studied.[10] Lorenz et al. have reported that the reaction of $[(PPh_3)_2Pt(C_2H_4)]$ with thiirane *S*-oxide afforded the corresponding disulfur dioxide complex $[(PPh_3)_2PtS_2O_2]$, which was characterized by elemental analysis and mass spectrometry, IR, and ^{31}P NMR spectroscopy.[11] However, synthesis of a disulfur complex $[(PPh_3)_2PtS_2]$ by the analogous reaction with thiirane was not successful.

Meanwhile, we have reported the synthesis of cyclic polychalcogenides containing a heavier main group element $[Tbt(R)ME_4]$ (M = Si, Ge, Sn, or Pb; E = S or Se; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl),[12] $[Tbt(R)MSe_2]$(M = Si or Sn),[12a,b, 13] and $[TbtSbS_n]$ ($n = 5$, 7)[14] by taking advantage of the extremely bulky substituent, the Tbt group. On the basis of these results, we envisioned that the introduction of this bulky substituent onto a phosphorus atom which should coordinate to platinum centers might be useful for the synthesis of novel classes of platinum polychalcogenido complexes. Here, we report the synthesis and characterization of the first mononuclear disulfur and diselenium complexes of platinum by utilizing extremely bulky phosphane ligands bearing a Tbt or 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) group.

Bulky phosphane ligands **1** were readily prepared by the treatment of a THF solution of ArLi (Ar = Tbt, Bbt) with an equimolar amount of phosphorous trichloride followed by the addition of a solution of MeLi (2.2 equiv) in diethyl ether (Scheme 1).[15] Reaction of **1a**,**b** with K_2PtCl_4 in benzene/H_2O at room temperature for 7 days afforded gray precipitates of *trans*-$[(ArMe_2P)_2PtCl_2]$ (**2a**,**b**), which were hardly soluble in common organic solvents except for chloroform. When platinum dichlorides **2a**,**b** were reduced by an excess of lithium naphthalenide (LiNp) in THF and the resulting platinum(0) species $[(ArMe_2P)_2Pt]$ (**3a**,**b**)[16] were successively treated with elemental sulfur (3 equiv as S), the first platinum disulfur complexes $[(ArMe_2P)_2PtS_2]$ (**4a**,**b**) were obtained as major products together with $ArMe_2P{=}S$ and a trace amount of unidentified platinum polysulfido complexes, which could be converted into **4a**,**b** by further treatment with triphenylphosphane. The structures of **4a**,**b** were identified by mass spectrometry, elemental analysis, and multinuclear NMR spectroscopy, and the molecular structure of **4b** was determined by X-ray crystallographic analysis (Figure 1 and Table 1).[17]



Scheme 1. Syntheses of disulfur and diselenium complexes of platinum, **4** and **5**. See text for full details.

The formation of **4a**,**b** having a novel PtS_2 ring system is in sharp contrast to the reaction of $[(Ph_3P)_4Pt]$ and $[(dppe)_2Pt]$

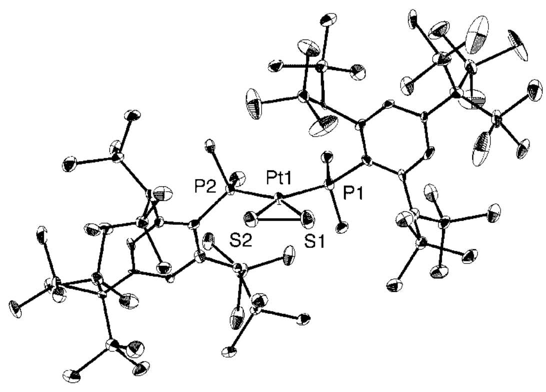


Figure 1. ORTEP drawing of **4b** with thermal ellipsoids set at 50% probability.

---

[*] Prof. Dr. N. Tokitoh, K. Nagata, Dr. N. Takeda
Institute for Chemical Research
Kyoto University
Gokasho, Uji, Kyoto 611-0011 (Japan)
Fax: (+81) 774-38-3209
E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp

[**] This work was partially supported by Grants-in-Aid for COE Research on Elements Science (No. 12CE2005) and Scientific Research on Priority Areas (A) (No. 11166250) from Ministry of Education, Culture, Sports, Science, and Technology of Japan. We thank Shin-Etsu Chemical Co., Ltd. for the generous gift of chlorotrimethylsilane.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

Table 1. Selected bond lengths [Å] and angles [°] for **4b** and **5b**.

4b		**5b**	
	Bond lengths		
Pt1-S1	2.348(3)	Pt1-Se1	2.4491(10)
Pt1-S2	2.337(3)	Pt1-Se2	2.4658(10)
S1-S2	2.077(3)	Se1-Se2	2.3363(11)
Pt1-P1	2.271(2)	Pt1-P1	2.271(2)
Pt1-P2	2.265(3)	Pt1-P2	2.261(2)
	Bond angles		
S1-Pt1-S2	52.63(9)	Se1-Pt1-Se2	56.76(3)
Pt1-S1-S2	63.41(11)	Pt1-Se1-Se2	61.98(3)
Pt1-S2-S1	63.96(11)	Pt1-Se2-Se1	61.26(3)
P1-Pt1-S1	102.07(9)	P1-Pt1-Se1	95.44(6)
P2-Pt1-S2	98.47(9)	P2-Pt1-Se2	99.94(6)
P1-Pt1-P2	106.87(8)	P1-Pt1-P2	107.85(7)

with elemental sulfur giving the corresponding tetrasulfido complexes, $[(Ph_3P)_2PtS_4]$ and $[(dppe)PtS_4]$, respectively.[7a] The diselenium analogues $[(ArMe_2P)_2PtSe_2]$ (**5a**,**b**), the first platinum diselenium complexes, were also obtained when elemental selenium was used instead of elemental sulfur as shown in Scheme 1. In contrast to the synthesis of **4**, complexes **5** were produced without any other platinum products, but the differences in reactivity of **3** toward sulfur and selenium are unclear at present. The structure of **5b** was also determined by X-ray crystallographic analysis (Figure 2, Table 1).[17]

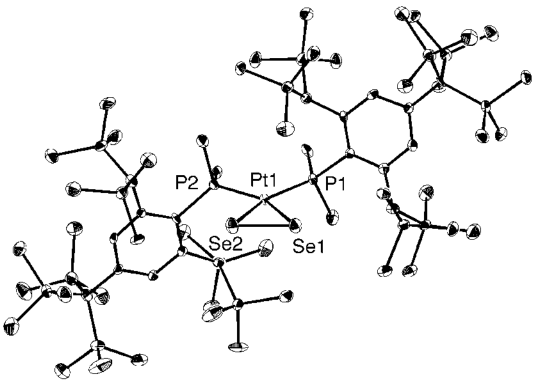


Figure 2. ORTEP drawing of **5b** with thermal ellipsoids set at 50% probability.

Crystallographic analysis showed that **4b** and **5b** are isomorphous and their geometries are very similar. In both cases, the platinum atoms have approximately square-planar geometries and the two Bbt groups are situated in *trans* position with regard to the P_2PtE_2 (E = S, Se) plane to decrease the steric congestion. The E1–E2 bond lengths and the E1-Pt1-E2 bond angles of the PtE_2 (E = S, Se) rings are similar to those of other ME_2 complexes, for example, $[IrS_2(dppe)_2]^+$ 2.066(6) Å, 50.8(2)°,[18] $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(S_2)(\mu\text{-}dppm)_2]$ 2.13(1) Å, 51.8(3)°,[19] $[(TpTP)TiS_2]$ 2.042(3) Å, 52.79(9)° (TpTP = tetra-*p*-tolylporphyrin),[20] $[Os\text{-}Se_2(CO)_2(PPh_3)_2]$ 2.321(1) Å, 54.23(2)°,[21] and $[IrSe_2(dppe)_2]^+$ 2.312(3) Å, 54.3(1)°.[22] The Pt–E (E = S, Se) and Pt–P bond lengths are close to those for platinum tetrachalcogenido complexes (2.35 (av.), 2.45 (av.), and 2.26 (av.) Å for Pt–S, Pt–Se, and Pt–P, respectively).[7b, 8, 23] The average of the two Pt–Se bond lengths in **5b** is 0.12 Å longer than the average Pt–S bond length in **4b**, and the Se–Se bond of **5b** is 0.26 Å longer than the S–S bond of **4b**. These differences in the bond lengths correlate well with the approximately 0.13 Å larger covalent radius of selenium than that of sulfur.[24] It is noteworthy that the P1-Pt1-P2 bond angles are somewhat larger than those for other related platinum polychalcogenido complexes, for example $[(dppe)PtS_4]$ 86.8(1)°,[23] $[(Ph_3P)_2PtS_4]$ 99.3(2)°,[7b] $[(Ph_3P)_2Pt(S_3O)]$ 98.47(8)°,[25] $[Pt_2(\mu\text{-}S)_2(dppy)_4]$ 102.98(6)° (dppy = 2-diphenylphosphinopyridine),[26] $[(dppe)PtSe_4]$ 86.31(20)°,[8a] $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ 99.6(1)°,[27] and an analogous dioxygen complex, $[(Ph_3P)_2PtO_2]$ 100–101°,[9] which reflects the severe steric repulsion between two Bbt groups. We assume that these larger P1-Pt1-P2 angles of **4b** and **5b** contribute to the stabilization of the three-membered PtE_2 ring systems.[28]

The ^{195}Pt NMR signals of **4b** and **5b** were observed at $\delta = -4983$ ($^1J_{Pt,P} = 3909$ Hz) and $\delta = -5030$ ($^1J_{Pt,P} = 3865$ Hz, $^1J_{Pt,Se} = 262$ Hz), respectively. In the ^{77}Se NMR spectrum of **5b**, only one broad signal was observed at $\delta = 582$ (see Supporting Information), although the satellite peaks arising from the ^{77}Se–^{195}Pt couplings could not be recognized probably because of broadening of the peak. This ^{77}Se resonance is slightly upfield relative to those for ^{77}Se atoms bound to the platinum in $PtSe_4$ rings, $[(dppe)PtSe_4]$ $\delta = 640$[8a] and $[Pt(Se_4)_3^{2-}]$ $\delta = 680$.[29]

Compounds **4** and **5** are both air-stable in the solid state, while they decomposed to the corresponding phosphane chalcogenides and metallic platinum on standing in solution at room temperature for several days.

In conclusion, we successfully prepared the first disulfur and diselenium complexes of platinum **4** and **5** by the reaction of platinum(0) complexes coordinated by monodentate bulky phosphane ligands bearing a Tbt or Bbt group with elemental sulfur and selenium, respectively, and their molecular structures were determined.

Experimental Section

4b: A THF suspension (3 mL) of *trans*-$[(BbtMe_2P)_2PtCl_2]$ (**2b**; 123 mg, 0.075 mmol) was treated with a THF solution of lithium naphthalenide (0.82 M, 0.37 mL, 4 equiv) at −78 °C. The reaction mixture was stirred for 1 h while being warmed to room temperature. After stirring for 1 h at room temperature, the solution of $[(BbtMe_2P)_2Pt]$ (**3b**) thus obtained was cooled to −78 °C and treated with S_8 (7.2 mg, 0.028 mmol, 3 equiv based on S). The reaction mixture was stirred for 4 h while being warmed to room temperature. After removal of the solvent, chloroform was added to the residue and the mixture was filtered through Celite. The filtrate was evaporated, and the crude product was dissolved in chloroform (3 mL). The solution was treated with triphenylphosphane (39 mg, 0.15 mmol) at 50 °C for 1.5 h, and the solvent was evaporated. The residue was purified by preparative gel permeation liquid chromatography (eluting with $CHCl_3$) to afford **4b** as a pure pale purple crystalline solid (86 mg, 71 %) along with $BbtMe_2P{=}S$ (11 mg, 10 %); **4b**: m.p. 162.3–163.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) $\delta = 0.16$ (s, 72 H), 0.21 (s, 54 H), 2.19 (br m, 12 H), 3.32 (s, 4 H), 6.65 (s, 4 H); ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C, 85 % H_3PO_4) $\delta = -32.2$ ($^1J_{P,Pt} = 3909$ Hz); ^{195}Pt NMR (64 MHz, $CDCl_3$, 25 °C, Na_2PtCl_6) $\delta = -4983$ (d, $^1J_{PtP} = 3909$ Hz); FAB MS: 1628 [M^+]; elemental analysis calcd (%) for $C_{64}H_{146}P_2PtS_2Si_{14}$: C 47.15, H 9.03; found: C 47.09, H 9.28.

5b: Using the same procedure as that for **4b** without the treatment of the crude products with triphenylphosphane, **5b** was obtained as a green crystalline solid (60 mg, 70 %) from **2b** (82 mg, 0.050 mmol) and elemental selenium (12 mg, 0.150 mmol); **5b**: m.p. 170.6–171.8 °C; ^{1}H NMR

(300 MHz, $CDCl_3$, 25 °C) $\delta = 0.17$ (s, 72 H), 0.22 (s, 54 H), 2.23 (br m, 12 H), 3.33 (s, 4 H), 6.64 (s, 4 H); ^{31}P NMR (120 MHz, $CDCl_3$, 25 °C, 85 % H_3PO_4) $\delta = -44.1$ ($^1J_{P,Pt} = 3865$ Hz); ^{77}Se NMR (57 MHz, $CDCl_3$, 25 °C) $\delta = 582$; ^{195}Pt NMR (64 MHz, $CDCl_3$, 25 °C, Na_2PtCl_6) $\delta = -5030$ (dd, $^1J_{Pt,P} = 3865$ Hz, $^1J_{Pt,Se} = 262$ Hz); FAB MS: 1723 [M^+]; elemental analysis calcd (%) for $C_{64}H_{146}P_2PtSe_2Si_{14}$: C 44.59, H 8.54; found: C 44.32, H 8.59.

Received: September 10, 2001 [Z 17879]

---

[1] For reviews on transition metal polychalocogenido complexes, see: a) J. W. Kois, *Coord. Chem. Rev.* **1990**, *105*, 195; b) M. A. Ansari, J. A. Ibers, *Coord. Chem. Rev.* **1990**, *100*, 223; c) M. R. Dubois, *Chem. Rev.*, **1989**, *89*, 1; d) J. Wacher, *Angew. Chem.* **1989**, *101*, 1645; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1613; e) A. Müller, E. Diemann, *Adv. Inorg. Chem.* **1987**, *89*, 31; f) D. Coucouvanis, A. Hadjikyriacou, M. Draganjac, M. G. Kanatzidis, O. Ileperuma, *Polyhedron* **1986**, *5*, 349; g) A. Müller, *Polyhedron* **1986**, *5*, 323; h) M. Draganjac, T. B. Rauchfuss, *Angew. Chem.* **1985**, *97*, 745; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 742; i) A. Müller, E. Diemann, R. Jostes, H. Bögge, *Angew. Chem.* **1981**, *93*, 957; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 934.

[2] A. Müller, W. Jaegermann, J. H. Enemark, *Coord. Chem. Rev.* **1982**, *46*, 245, and references therein.

[3] a) R. F. Borch, M. E. Pleasants, *Proc. Natl. Acad. Sci. USA* **1979**, *76*, 6611; b) W. Weigand, R. Wünsch, S. Dick, *Z. Naturforsch. B* **1996**, *51*, 1511; c) M. I. Djuran, E. L. M. Lempers, J. Reedijk, *Inorg. Chem.* **1991**, *30*, 2648; d) S. J. Berners-Price, P. W. Kuchel, *Inorg. Biochem.* **1990**, *38*, 305; e) E. L. M. Lempers, K. Inagaki, J. Reedijk, *Inorg. Chim. Acta* **1988**, *152*, 201; f) V. K. Jain, *Inorg. Chim. Acta* **1987**, *133*, 261; g) B. Odenheimer, W. Wolf, *Inorg. Chim. Acta* **1982**, *66*, L41.

[4] P. Li, M. D. Curtis, *Inorg. Chem.* **1990**, *29*, 1242, and references therein.

[5] a) F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley-Interscience, New York, **1988**, Chap. 13 and 30; b) N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, UK, **1984**, Chap. 15 and 16.

[6] a) K. A. Hofmann, F. Höchtlen, *Ber.* **1903**, *36*, 3090; b) P. E. Jones, J. Katz, *J. Chem. Soc. Chem. Commun.* **1967**, 842.

[7] a) J. Chatt, D. M. P. Mingos, *J. Chem. Soc. A* **1970**, 1243; b) D. Dudis, J. P. Fackler, Jr., *Inorg. Chem.* **1982**, *21*, 3578; c) R. R. Gukathasan, R. H. Morris, A. Walker, *Can. J. Chem.* **1983**, *61*, 2490.

[8] a) M. R. Lewtas, C. P. Morley, M. Di Vaira, *Polyhedron* **2000**, *19*, 751; b) S. Ford, M. R. Lewtas, C. P. Morley, M. Di Vaira, *Eur. J. Inorg. Chem.* **2000**, 933.

[9] a) C. D. Cook, P.-T. Cheng, S. C. Nyburg, *J. Am. Chem. Soc.* **1969**, *91*, 2123; b) T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, N. Hagihara, *Chem. Commun.* **1969**, 743; c) P.-T. Cheng, C. D. Cook, S. C. Nyburg, K. Y. Wan, *Can. J. Chem.* **1971**, *49*, 3772.

[10] J. S. Valentine, *Chem. Rev.* **1973**, *73*, 235.

[11] I.-P. Lorenz, J. Kull, *Angew. Chem.* **1986**, *98*, 276; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 261.

[12] a) N. Tokitoh, R. Okazaki, *Adv. Organomet. Chem.* **2001**, *47*, 121; b) R. Okazaki, N. Tokitoh, *Acc. Chem. Res.* **2000**, *33*, 625; c) N. Tokitoh, N. Kano, K. Shibata, R. Okazaki, *Organometallics* **1995**, *14*, 3121; d) T. Matsumoto, N. Tokitoh, R. Okazaki, M. Goto, *Organometallics* **1995**, *14*, 1008; e) Y. Matsuhashi, N. Tokitoh, R. Okazaki, M. Goto, S. Nagase, *Organometallics* **1993**, *12*, 1351; f) N. Tokitoh, H. Suzuki, T. Matsumoto, Y. Matsuhashi, R. Okazaki, M. Goto, *J. Am. Chem. Soc.* **1991**, *113*, 7047.

[13] a) N. Tokitoh, *Phosphorous Sulfur and Silicon*, **1998**, *136–138*, 123; b) M. Saito, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **1997**, *119*, 11 124.

[14] N. Tokitoh, Y. Arai, J. Harada, R. Okazaki, *Chem. Lett.* **1995**, 959.

[15] Since phosphanes **1** were very air-sensitive in solution, **1** could not be obtained in a pure state because of the contamination with trace amounts of oxidized $ArMe_2P{=}O$ during the course of workup and purification. However, the structures of **1** were identified by NMR spectroscopy and high resolution mass spectrometry (HRMS calcd for **1b**; $C_{32}H_{73}PSi_7$: 684.3835; found 684.3837).

[16] The intermediates **3a,b** could be identified by ^{31}P NMR spectroscopy (120 MHz, C_6D_6, 25 °C, relative to 85 % H_3PO_4) **3a**: $\delta_P = 0.9$, $^1J_{P,Pt} = 3974$ Hz, **3b**: $\delta_P = 3.7$, $^1J_{P,Pt} = 3869$ Hz. These values are in the range typical for those of $[Pt(PR_3)_n]$ complexes; B. E. Mann, A. Musco, *J. Chem. Soc. Dalton Trans.* **1980**, 776.

[17] Crystallographic data for **4b** and **5b**. **4b**: $C_{64}H_{146}P_2PtS_2Si_{14}$, $M = 1630.22$, monoclinic, space group *Cc* (no. 9), $a = 40.121(8)$, $b = 9.130(3)$, $c = 23.740(6)$ Å, $\beta = 91.2201(19)°$, $V = 8694(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.245\ g\,cm^{-3}$, $\mu = 19.3\ cm^{-1}$, R_1 (wR_2) = 0.062 (0.146), $T = 93(2)$ K, GOF = 1.00. **5b**: $C_{64}H_{146}P_2PtSe_2Si_{14}$, $M = 1724.02$, monoclinic, space group *Cc* (no. 9), $a = 40.213(2)$, $b = 9.1551(15)$, $c = 23.860(2)$ Å, $\beta = 89.0303(7)°$, $V = 8782.8(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.304\ g\,cm^{-3}$, $\mu = 26.9\ cm^{-1}$, R_1 (wR_2) = 0.047 (0.127), $T = 93(2)$ K, GOF = 1.08. The intensity data were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å). The structures were solved by direct methods with SIR-97. The three methyl carbon atoms of the one trimethylsilyl group on the Bbt group are disordered in **4b**. In Figure 1, the minor part of the disordered carbon atoms is omitted for clarity. The P_2PtSe_2 plane and the four methyl carbon atoms bound to each phosphorus atom is disordered in **5b**. In Figure 2, the major orientation (96 %) is represented. All non-hydrogen atoms (except for the minor parts of the disordered moieties in the cases of **4b** and **5b**) were refined anisotropically. The final cycles of full-matrix least-squares refinement were based on 16 756 (**4b**) and 14 928 (**5b**) observed reflections (all data) and 761 (**4b**) and 821 (**5b**) variable parameters, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-169659 (**4b**) and -169660 (**5b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[18] W. D. Bonds, Jr., J. A. Ibers, *J. Am. Chem. Soc.* **1972**, *94*, 3413.

[19] J. Kuncheria, H. A. Mirza, H. A. Jenkins, J. J. Vittal, R. J. Puddephatt, *J. Chem. Soc. Dalton Trans.* **1998**, 285.

[20] a) C. Ratti, P. Richard, A. Tabard, R. Guilard, *J. Chem. Soc. Chem. Commun.* **1989**, 69; b) R. Guilard, C. Ratti, A. Tabard, P. Richard, D. Dubois, K. M. Kadish, *Inorg. Chem.* **1990**, *29*, 2532.

[21] D. H. Farrar, K. R. Grundy, N. C. Payne, W. R. Roper, A. Walker, *J. Am. Chem. Soc.* **1979**, *101*, 6577.

[22] A. P. Ginsberg, W. E. Lindsell, C. R. Sprinkle, K. W. West, R. L. Cohen, *Inorg. Chem.* **1982**, *21*, 3666.

[23] C. E. Briant, M. J. Calhorda, T. S. A. Hor, N. D. Howells, D. M. P. Mingos, *J. Chem. Soc. Dalton Trans.* **1983**, 1325.

[24] L. Pauling, *The Chemical Bond*, Cornell University, Ithaca, NY, **1967**, p. 136.

[25] A. Shaver, M. El-khateeb, A.-M. Lebuis, *Angew. Chem.* **1996**, *108*, 2510; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2362.

[26] V. W.-W. Yam, P. K.-Y. Yeung, K.-K. Cheung, *J. Chem. Soc. Chem. Commun.* **1995**, 267.

[27] A. Bencini, M. Di Vaira, R. Morassi, P. Stoppioni, F. Mele, *Polyhedron* **1996**, *15*, 751.

[28] As for dioxygen complexes of palladium and platinum, Otsuka has reported that modified INDO calculations for $[(H_3P)_2MO_2]$ (M = Pd, Pt) showed a minimum of the total energy at the P-M-P bond angle of 107°; S. Otsuka, *J. Organomet. Chem.* **1980**, *200*, 191.

[29] M. A. Ansari, J. A. Ibers, *Inorg. Chem.* **1989**, *28*, 4068.