be sufficient to account for the preference of the axial form of $Os(CO)_4(AsPh_3)$ over the equatorial isomer. Experiments are currently under way in an attempt to distinguish between these two possible explanations for the switchover.

Acknowledgment. We are grateful to the National Sciences and Engineering Council of Canada for financial support.

Registry No. *ax*-$Fe(CO)_4(PPh_3)$, 35679-07-3; *ax*-$Fe(CO)_4(AsPh_3)$, 35644-25-8; *ax*-$Fe(CO)_4(SbPh_3)$, 35917-16-9; *ax*-$Ru(CO)_4(PPh_3)$, 33635-52-8; *eq*-$Ru(CO)_4(AsPh_3)$, 85781-13-1; *ax*-$Ru(CO)_4(AsPh_3)$, 85848-64-2; *eq*-$Ru(CO)_4(SbPh_3)$, 71356-99-5; *ax*-$Ru(CO)_4(SbPh_3)$, 85848-65-3; *ax*-$Os(CO)_4(PPh_3)$, 33635-53-9; *eq*-$Os(CO)_4(AsPh_3)$, 85781-14-2; *ax*-$Os(CO)_4(AsPh_3)$, 85848-66-4; *eq*-$Os(CO)_4(SbPh_3)$, 85781-15-3; *ax*-$Os(CO)_4(SbPh_3)$, 85848-67-5; $Ru(CO)_5$, 16406-48-7; $Os(CO)_5$, 16406-49-8.

Supplementary Material Available: Listings of final positional and thermal parameters with standard deviations for $Ru(CO)_4(AsPh_3)$ and $Os(CO)_4(SbPh_3)$ (4 pages). Ordering information is given on any current masthead page.

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[23] These calculations did not allow for reorientation of the atoms within the molecule so as to minimize these contacts.

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A Dinuclear Platinum(II) Complex Containing a Bridging Tridentate Triphosphorous Acid Derivative $[((EtO)_2PO)_2P(O)]^-$

Sir:

The reactivity of P–OR and P–Cl bonds is such that reactions between triorgano phosphites or chlorophosphines and transition-metal complexes may often cause a transformation of the phosphorus donor ligand as well as the expected coordination. Examples are the well-documented degradation of triorgano phosphites, $[P(OR)_3]$, to phosphonato ligands, $P(O)(OR)_2$,[1] and the recent transformation of trimethyl phosphite to the unusual $P(OMe)_2$[2,3] and $P(OMe)$[4] ligands. Reactions in which phosphorus(III) compounds condense and coordinate to form diphosphito ligands are also known, for example, in the formation of the bidentate bridging diphosphito ligand $-O_2POPO_2-$ from the solid-state reaction of phosphorous acid with a platinum(II) salt.[5] A very recent communication[6] also advances evidence for the formation of higher homologues of this ligand, but fully characterized examples involving more than two condensed phosphorus units are unknown. Indeed tri- and polyphosphites are very rare even in simple phosphorus chemistry.[7] We now wish to report that in the course of studying the reactions of tetraethyl diphosphite, $[(EtO)_2POP(OEt)_2]$, and of chlorodiethoxyphosphine, $[PCl(OEt)_2]$, with platinum complexes we have established the formation of a ligand derived from the unknown triphosphorous acid, $[H_5P_3O_7]$.

Addition of $[(EtO)_2POP(OEt)_2]$ (0.10 mL) to a stirred solution of *trans*-$[Pt_2Cl_4(PEt_3)_2]$ (0.30 g) in dichloromethane (15 mL) at 25 °C under an atmosphere of dry nitrogen,

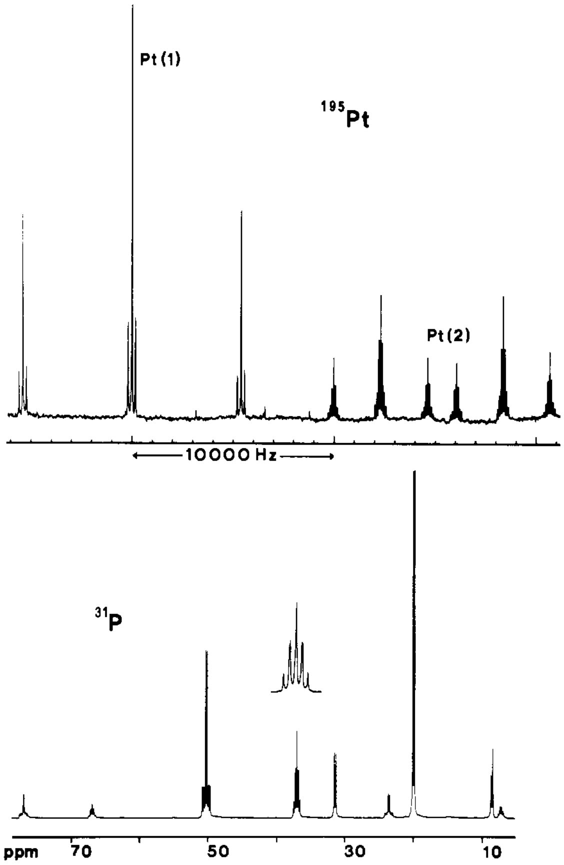

Figure 1. $^{195}Pt\{^1H\}$ and $^{31}P\{^1H\}$ nuclear magnetic resonance spectra of complex **1**.

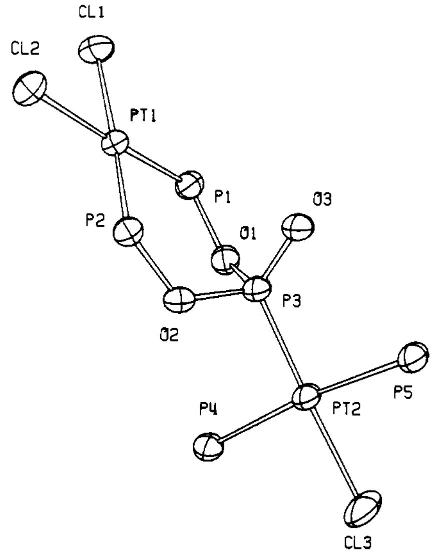

Figure 2. ORTEP plot of the molecular structure of complex **1**. The ethoxy groups on P(1) and P(2) and the ethyl groups on P(4) and P(5) have been omitted for clarity.

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[1] Pidcock, A.; Waterhouse, C. R. *J. Chem. Soc. A* **1970**, 2080.

[2] Choi, H. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 153.

[3] Day, V. W.; Tavanaiepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657.

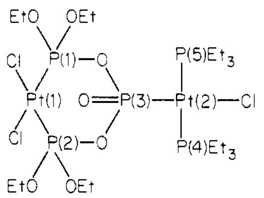
[4] Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1981**, 2250.

[5] Sperline, R.; Dickson, M. K.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* **1977**, 62. Dos Remedios Pinto, M. A. F.; Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A.; Kuroda, R. *J. Chem. Soc., Chem. Commun.* **1980**, 13.

[6] Dickson, M. K.; Fordyce, W. A.; Appel, D. M.; Alexander, K.; Stein, P.; Roundhill, D. M. *Inorg. Chem.* **1982**, *21*, 3857.

[7] Toy, A. D. F. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; Vol. 2, p 475.

followed by evaporation of solvent and recrystallization of the residues from CH_2Cl_2/hexane, gave complex **1** as colorless crystals (0.13 g). The same product can be obtained by hydrolysis of *cis*-$[PtCl_2(PCl(OEt)_2)(PEt_3)]$ using aqueous HCl in acetone, but the course of this latter reaction is very sensitive to water and HCl concentration and the simple *cis*-$[PtCl_2(P(OH)(OEt)_2)(PEt_3)]$ is also a product. The basic form of **1** and the presence of the bridging triphosphite ligand was inferred from $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra (Figure 1) and subsequently confirmed by an X-ray crystal structure determination (Figure 2).



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In the $^{31}P\{^1H\}$ NMR spectrum[8] the resonance at +20.0 ppm is assigned to the triethylphosphine ligands, P(4,5), and their mutually trans arrangement on a platinum(II) center is indicated by the magnitude of coupling to ^{195}Pt ($I = ^1/_2$, 34% abundance), ^1J(Pt-P) = 2322 Hz. The presence of P(3) in a cis relationship to the PEt_3 ligands is shown by the 1:1 doublet form of the P(4,5) resonance with ^2J(P-P) = 26 Hz. The P(1,2) resonance centered at +50.3 ppm is associated with both direct (^1J(Pt-P) = 5408 Hz) and indirect (^3J(Pt-P) = 94 Hz) coupling to ^{195}Pt, the former value being typical of those found by us for a phosphite trans to chlorine, and is also coupled to a single phosphorus nucleus P(3) (^2J(P-P) = 22 Hz). This suggests the bridging arrangement, which is confirmed by the P(3) resonance at +37.0 ppm, which has the form expected for indirect coupling to two sets of equivalent pairs of ^{31}P nuclei and direct coupling to a single platinum (^1J(Pt-P) = 6064 Hz). Interestingly, P(3) is not significantly coupled to Pt(1).

The $^{195}Pt\{^1H\}$ NMR spectrum[9] confirmed the presence of two nonequivalent platinum nuclei (Pt(1), Ξ = 21.403838 MHz; Pt(2), Ξ = 21.397700 MHz) with couplings to phosphorus as expected from the above analysis and with ^4J(Pt-Pt) = 363 Hz.

Crystals of **1** suitable for study by X-ray diffraction were obtained by crystallization from a dichloromethane/pentane solvent mixture.[10] Figure 2 shows that the overall structure is dictated by the six-membered ring linking the two platinum(II) centers. The ring lies in a *chaise-longue* conformation with O(1) and O(2) held in the same plane as the Pt(1) coordination. P(3) lies above this plane, and the Pt(2) coordination plane is approximately perpendicular (93.6°) to that of Pt(1). As expected, the shortest phosphorus-oxygen distance is the P(3)-O(3) double bond, 1.471 (9) Å. There are significant differences between the various P-O single bonds, with P^V-O(1,2), P^{III}-O(1,2), and P^{III}-OEt averaging 1.637 (9), 1.601 (8), and 1.565 (11) Å, respectively, but the Pt-P bonds do not appear to show any comparable effects. Thus, Pt(1)-P(1,2) averages 2.204 (3) Å and Pt(2)-P(3) is 2.198 (3) Å.

Our research is continuing in the designed synthesis of condensed phosphites, and full details will be published at a later date.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for research grants, K. Beveridge for technical assistance during the crystal structure determination, and the University of Sussex for a study leave (A.P.).

Registry No. **1**, 85762-22-7; $(EtO)_2POP(OEt)_2$, 21646-99-1; *trans*-$[Pt_2Cl_4(PEt_3)_2]$, 17522-94-0; *cis*-$[PtCl_2(PCl(OEt)_2)(PEt_3)]$, 85762-23-8.

Supplementary Material Available: Tables of fractional atomic coordinates and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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[8] $^{31}P\{^1H\}$ NMR spectra were recorded at 101.3 MHz, and chemical shifts are quoted in ppm (high field negative) relative to 85% H_3PO_4.

[9] $^{195}Pt\{^1H\}$ NMR spectra were recorded at 53.5 MHz and chemical shifts (Ξ) are quoted in MHz standardized to $[Si(CH_3)_4]$ at 100 MHz.

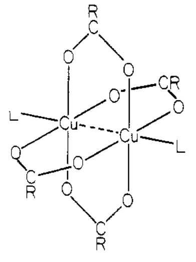
[10] The colorless crystals of the title compound, $C_{20}H_{50}Cl_3O_7P_5Pt_2$, are monoclinic, space group $P2_1/c$, with a = 17.547 (8) Å, b = 19.775 (6) Å, c = 11.268 (3) Å, β = 106.42 (3)°, V = 3750 (2) Å^3, Z = 4, and ρ_{calcd} = 1.867 g cm^{-3} (Mo Kα = 0.71069 Å). The structure was solved and refined with use of 4646 independent reflections ($I > 0$) measured on a Picker four-circle diffractometer automated with a PDP-11/10 computer. The measurements were for two octants in the range 2θ = 0-45°. The platinum atoms were located by direct methods, and the structure was then developed and refined by Fourier difference maps and the method of least squares, anisotropic thermal corrections being applied to all non-hydrogen atoms. The crystal structure is molecular. Convergence (maximum shift/esd = 0.12) was attained at R = 0.0612, R_w = 0.0726. The final difference map had no interpretable peaks (maximum 1.83 e Å^{-3} near Pt).

A Novel Variation on a Classical Dimeric Structure Type. Preparation and Structure of the Metal-Nitroxyl Complex $[Cu(O_2CCCl_3)_2(Tempo)]_2$

Sir:

We wish to report the preparation and crystal structure of a compound whose molecular structure is an unusual variant of a classic dimeric structure type and which contains one of the few structurally characterized examples of a metal-coordinated nitroxyl function.

The bridged binuclear structure I, first documented in 1953 for copper(II) acetate monohydrate,[1] is ubiquitous in modern coordination chemistry. It is found not only for carboxylates of many transition elements[2] but also for dimers containing a wide variety of other triatomic bridging ligands.[3] This structure is associated with a spectrum of metal-metal interactions ranging from no bonding at all[5] through weak spin



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[1] van Niekerk, J. N.; Schoening, F. R. L. *Acta Crystallogr.* **1953**, *6*, 227.

[2] For a tabulation, see: Koh, Y. B.; Christoph. G. G. *Inorg. Chem.* **1979**, *18*, 1122.

[3] A recent discussion and tabulation of such bridging ligands may be found in ref 4, pp 26-29.

[4] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

[5] Larin, G. M.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T.; Pasnskii, A. A.; Kolobova, N. E. *J. Organomet. Chem.* **1971**, *27*, 53.

0020-1669/83/1322-1962$01.50/0