to MeCN, a slow reaction with the solvent occurs and the solution develops an absorption spectrum[22] that is analogous to that for impure $(Me_4N)O_2$ samples in MeCN.

If a one-to-one combination of H_2O_2 and $(Me_4N)OH\cdot H_2O$ is added to MeCN, the solution immediately exhibits a strong absorption band at 290 nm [purportedly due to the dimer of $(Me_4N)O_2$ in the previous study][20] as well as a band at 254 nm. Addition of H_2O causes the 290-nm band to disappear and the 256-nm band to increase proportionately (there is an isosbestic point at 267 nm). Neither solution contains any $O_2^{\bullet-}$ on the basis of ESR and electrochemical measurements.

The ESR spectra for authentic pure $(Me_4N)O_2$[21] dissolved in MeCN and Me_2SO are similar to those reported previously for electrogenerated $O_2^{\bullet-}$.[3,4,20] Magnetic susceptibility measurements of $(Me_4N)O_2$ (synthesized by the new procedure)[21] indicate that it is about 93% pure [KO_2 (96%) used as the reference standard]. The magnetic moments (corrected for diamagnetism) for KO_2 and $(Me_4N)O_2$ are 1.89 ± 0.05 μ_B for each material.

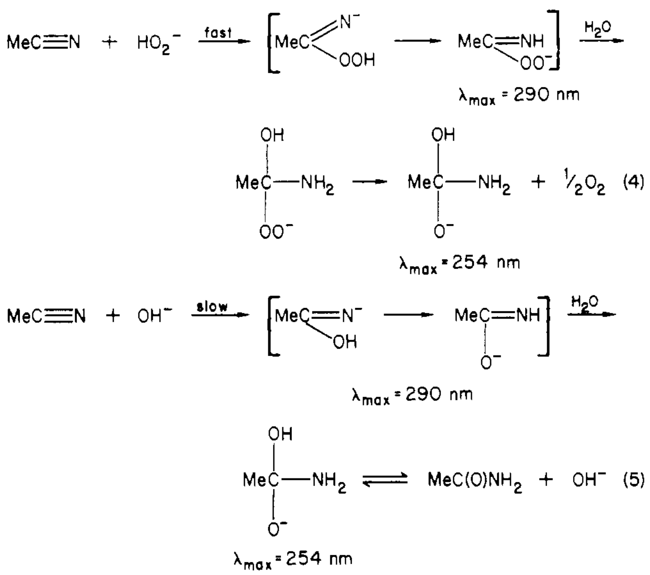
Figure 1 illustrates the cyclic voltammograms for O_2 and $(Me_4N)O_2$ in MeCN and Me_2SO. On the basis of the voltammetric peak currents[20,23] the solid $(Me_4N)O_2$ (93% pure), when dissolved in MeCN, yields 60-80% electroactive $O_2^{\bullet-}$ and, in Me_2SO, 70-90% $O_2^{\bullet-}$. This is in accord with the electrogeneration efficiencies for $O_2^{\bullet-}$ in MeCN and Me_2SO and reflects the respective stability of $O_2^{\bullet-}$ in these solvents.

The water-induced formation of HO_2^- from $O_2^{\bullet-}$,[6-9,13] the attack by HO_2^- and OH^- of acetonitrile,[13,26] and the subsequent hydrolysis of the adducts are outlined by eq 1-5.

$$O_2^{\bullet-} + H_2O \rightleftarrows HO_2\cdot + OH^- \qquad pK_a = 4.88 \qquad (1)$$

$$O_2^{\bullet-} + HO_2\cdot \rightarrow O_2 + HO_2^- \qquad k_2 = 1.0 \times 10^8\ M^{-1}\ s^{-1} \qquad (2)$$

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O \qquad pK_a = 11.8 \qquad (3)$$



The coincidence of the 254-nm absorption bands for $O_2^{\bullet-}$ and $MeC(OH)(O^-)NH_2$ in MeCN precludes spectrophotometric assays for superoxide ion. Either magnetic susceptibility measurements of the solid salts or voltammetric measurements of $O_2^{\bullet-}$ solutions (Figure 1) are recommended for reliable assays.

In summary, the original synthetic procedure[19,20] for $(Me_4N)O_2$ can yield an impure product that contains $(Me_4N)OOH$ and $(Me_4N)OH\cdot H_2O$ (slightly soluble in liquid ammonia). The UV-visible spectrum for pure $(Me_4N)O_2$ (synthesized by the new procedure) in MeCN is identical with that for $O_2^{\bullet-}$ produced by electrosynthesis from O_2 [λ_{max} = 253 nm ($\epsilon = 3.0 \pm 1.0$ mM^{-1} cm^{-1})]. The amount of $O_2^{\bullet-}$ that results from the dissolution of $(Me_4N)O_2$ in MeCN or Me_2SO makes it a more efficient source than electrosynthesis. The inefficiency of the latter process yields substantial amounts of OH^- and HO_2^- in the product solution.

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Registry No. $(Me_4N)O_2$, 3946-86-9; $[MeC(OO^-)=NH]$, 101032-83-1; $[MeC(O^-)(OH)NH_2]$, 101032-84-2; $(Me_4N)OH\cdot H_2O$, 55605-35-1; $(Me_4N)_2CO_3$, 40105-52-0; KO_2, 12030-88-5; $(Me_4N)O_2$, 3946-86-9; H_2O_2, 7722-84-1.

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(22) Private communication from Dr. D. Marrocco at Maxdem Corp., Pasadena, CA 91105, and observed in this laboratory.

(23) Sawyer, D. T.; Yamagushi, K. S.; Calderwood, T. S. "Electrochemical Generation of Superoxide Ion and Other Oxy Radicals". In *Handbook of Methods for Oxy Radicals Research*; Greenwald, R. A., Ed.; CRC Press: Cleveland, OH 1984.

(24) Gampp, H.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 357.

(25) Kim, S.; DiCosimo, R.; San Filippo, J., Jr. *Anal. Chem.* **1979**, *51*, 679.

(26) Sawaki, Y.; Ogata, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 793.

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Synthesis and Structural Characterization of Methylenebis(phosphinic acid) $(CH_2(PH(O)OH)_2)$

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Recently the binuclear tetraanionic complex tetrakis(μ-pyrophosphito)diplatinum(II) ($Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$) has attracted considerable interest because of its intense luminescence in aqueous solution at ambient temperature.[2] The triplet excited state is both a strong reductant and oxidant,[3] and it also reacts as a free radical to abstract a hydrogen atom from the C-H bond of both isopropyl alcohol and toluene.[4] The photophysics and photochemistry of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ have been explained on the basis of Gray's molecular orbital model, whereby a close separation between the $A_{1g}(d\sigma^*)$ and $A_{2u}(p_z)$ orbital levels on Pt_2 is induced by intermetallic interaction $A_{2u}(p_z)$ along the z axis.[5]

The extension and development of this chemistry requires the synthesis of new ligands. Pyrophosphorous acid is a hydrolytically unstable compound, which can be obtained in the pure state only with some difficulty.[6] Synthetic routes to μ-pyrophosphito complexes are thereby very limited; and indeed the synthesis of $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ circumvents these problems by effecting the condensation of phosphorous to pyrophosphorous acid as a template reaction with the precursor platinum complex. Such a method is not generally adaptable to other metal complexes. We therefore need a pyrophosphite analogue compound that has

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(1) (a) Tulane University. (b) Louisiana State University.

(2) Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061-7064. Markert, J. T.; Clements, D. P.; Corson, M. R.; Nagle, J. K. *Chem. Phys. Lett.* **1983**, *97*, 175-179. Bär, L.; Gliemann, G. *Chem. Phys. Lett.* **1984**, *108*, 14-17.

(3) Che, C.-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796-7797. Heuer, W. B.; Totten, M. D.; Rodman, G. S.; Hebert, E. J.; Tracy, H. J.; Nagle, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 1163-1164.

(4) Roundhill, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 4354-4356. Gray, H. B. Presented at the Biennial Inorganic Chemical Symposium, York University, June 1985.

(5) Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3553-3555.

(6) Schwarzmann, E.; Van Wazer, J. R. *J. Inorg. Nucl. Chem.* **1960**, *14*, 296-297.

0020-1669/86/1325-1290$01.50/0

Table I. Crystallographic Details for $CH_2(PH(O)OH)_2$

cryst dimens, mm	0.24 × 0.32 × 0.40
formula	$CH_6O_4P_2$
fw	144.0
space group	$P2_1/n$
a, Å	4.954 (3)
b, Å	10.334 (2)
c, Å	10.403 (2)
β, deg	94.16 (4)
Z	4
V, Å^3	531.2 (6)
ρ_{calcd}, g/cm^3	1.801
linear abs coeff, cm^{-1}	7.1
temp, °C	22
diffractometer	Enraf-Nonius CAD 4
radiation	graphite-monochromated Mo Kα (λ = 0.71073 Å)
colln range	$h,k,\pm l$
2θ limits	$1.0 \leq 2\theta \leq 32$
scan type	$\omega - 2\theta$
scan speed, s	max of 240 to give $I = 50\sigma(I)$
no. of unique data	1835
no. of unique data with $F_o^2 \geq 3\sigma(F_o^2)$	1425
no. of variables	88
$R(F)^a$	0.029
$R_w(F)^a$	0.036
residual, e Å^{-3}	0.47

$^a R = \sum|\Delta F|/\sum|F_o|$, and $R_w = [\sum w|\Delta F^2|/\sum w|F_o|^2]^{1/2}$.

Table II. Coordinates and Isotropic Thermal Parameters for $CH_2(PH(O)OH)_2$

atom	x	y	z	B_{eq} or B, Å^2
P1	0.32805 (8)	0.06558 (4)	0.68494 (4)	1.744 (6)
P2	0.32541 (8)	0.28179 (4)	0.48601 (4)	1.904 (7)
O1	0.6257 (2)	0.0444 (1)	0.6542 (1)	2.66 (2)
O2	0.2648 (3)	0.0364 (1)	0.8196 (1)	2.63 (2)
O3	0.6297 (2)	0.3151 (1)	0.4951 (1)	3.35 (3)
O4	0.2365 (3)	0.1849 (1)	0.3853 (1)	2.74 (2)
C	0.2574 (3)	0.2305 (2)	0.6450 (1)	2.06 (3)
H1P	0.184 (4)	−0.009 (2)	0.606 (2)	2.6 (4)
H2P	0.196 (3)	0.389 (2)	0.473 (1)	1.5 (3)
H10	0.648 (6)	−0.019 (3)	0.650 2)	6.0 (7)
H3O	0.651 (4)	0.353 (2)	0.458 (2)	4.2 (5)
H1C	0.079 (4)	0.249 (3)	0.660 (2)	3.9 (5)
H2C	0.365 (4)	0.279 (2)	0.707 (2)	3.7 (5)

a hydrolytically stable group between phosphorus nuclei and that is also amenable to chemical modification of this bridgehead group. Such a compound is methylenebis(phosphinic acid) ($CH_2(PH(O)OH)_2$). This compound minimizes variations to pyrophosphorous acid and has both hydroxylic acid and phosphoryl group substituents. Such a compound will allow complexes to be prepared that are stabilized by intramolecular hydrogen bonding, and the ligand periphery resembles complexes of *P*-pyrophosphite in being chemically suitable for the intercalation of any metal complexes into oxide or zeolite structures.

Experimental Section

The compound $CH_2(PCl_2)_2$ was prepared by the literature method.[7] All manipulations were carried out under nitrogen. Infrared spectra were measured on a Perkin-Elmer Model 683B spectrophotometer; ^1H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker AC 200 or on a JEOL FX60 spectrometer operating at 200.13, 15.08, and 81.02 MHz, respectively. Microanalyses were performed by Galbraith Laboratories, Inc.

Synthesis. Methylenebis(phosphinic acid) ($CH_2(PH(O)OH)_2$). A 240-mL three-necked round-bottom flask was mounted in an ice bath placed on a magnetic stirrer. A stir bar was placed inside the flask and 50 mL of water added. The flask was fitted with a dropping funnel containing $CH_2(PCl_2)_2$ (25 mL). The apparatus was purged with nitrogen and the $CH_2(PCl_2)_2$ added dropwise at the rate of 1–2 drops/s. The ice bath was removed and the mixture stirred for 1 h. Volatiles were removed on a rotary evaporator with the flask warmed in a water bath and the resulting oil dissolved in methanol (≈35 mL). Acetone was added to produce an oil and the supernatant discarded. The oil was redissolved in methanol and acetone added to produce a cloudiness. After crystallization further acetone was added, and the mixture was kept at 0 °C for 12–18 h. The white crystals were filtered and dried in vacuo. Yield is 95%. Anal. Calcd for $CH_6O_4P_2$: C, 8.33; H, 4.20; P, 43.0. Found: C, 8.55; H, 4.05; P, 42.6.

X-ray Structure. Data Collection and Structure Solution. A crystal of $CH_2(PH(O)OH)_2$ was sealed in a thin-walled glass capillary for protection against water vapor. The crystallographic details of the data collection are given in Table I. The atomic coordinates are given in Table II. The space group was unambiguously determined from systematic absences $h0l$ with l odd and $0k0$ with k odd. Data reduction included corrections for background, Lorentz–polarization, and absorption. The absorption corrections were made on the basis of ψ scans of reflections near χ = 90° by using program EAC of the Enraf-Nonius SDP.[8] The minimum value transmission factor was 94.75%.

The structure was solved by using MULTAN[9] and refined by full-matrix least squares based on F with weights $w = \sigma^{-2}(F_o)$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located from difference maps and refined isotropically. Atomic scattering factors were those of Cromer and Waber, with anomalous coefficients of Cromer.[10] No correction for extinction was necessary.

Results and Discussion

We have synthesized methylenebis(phosphinic acid) ($CH_2(PH(O)OH)_2$) in 95% yield by the hydrolysis of $CH_2(PCl_2)_2$ (prepared from CH_2Cl_2, Al, and PCl_3) (eq 1). Recrystallization from a methanol and acetone mixture gives the compound as colorless crystals. This synthetic approach follows the standard route for

$$CH_2(PCl_2)_2 + 4H_2O \rightarrow CH_2(PH(O)OH)_2 + 4HCl \quad (1)$$

the preparation of RPH(O)OH from $RPCl_2$.[11] The compound is soluble in water, methanol, DMF, and Me_2SO and is stable to boiling water for 1 h. The IR spectrum (KBr) shows the following bands: 3440 cm^{-1} (ν(OH)); 2960, 2910 cm^{-1} ($\nu(CH_2)$); 2460, 2420 cm^{-1} (ν(PH)); 1362 cm^{-1} ($\delta(CH_2)$); 1200, 1140, 1095, 1025, 1003, 955, 940 cm^{-1} (ν(P=O) and ν(P—O)). The following NMR parameters fully confirm the solution structure of the compound: $\delta(^1H)$ 2.56 (triplet of triplets, CH_2, $^2J(PH)$ = 17.6 Hz, $^3J(HH)$ = 2 Hz), 7.27 (doublet of triplets, PH, $^1J(PH)$ = 581 Hz, $^3J(HH)$ = 2 Hz); $\delta(^{13}C)$ 32.77 (triplet of triplet of triplets, $^1J(PC)$ = 79.7 Hz, $^1J(CH)$ = 125.7 Hz, $^2J(CH)$ = 20.5 Hz); $\delta(^{31}P)$ 23.0 (doublet of triplets, T_1 = 3.5 s)). The compound undergoes slow P–H exchange in D_2O solvent over a period of several hours at ambient temperature ($t_{1/2} \approx 2$ h) to give first $CH_2(PH(O)OD)(PD(O)OD)$ ($\delta(^{31}P)$ 22.98 (PH), 22.62 (PD, pseudo-triplet, $^1J(PD)$ = 87 Hz) and then $CH_2(PD(O)OD)_2$. Aqueous solutions of $CH_2(PH(O)OH)_2$ undergo slow oxidation over several days to $CH_2(PH(O)OH)(P(O)(OH)_2)$ ($\delta(^{31}P)$ 24.9 ($^1J(PH)$ = 578 Hz, $^2J(PP)$ = 8 Hz), 17.2 ($^2J(PH)$ = 17 Hz)) and then to methylenebis(phosphonic acid) (medronic acid, $CH_2(PH(O)(OH)_2)_2$, $\delta(^{31}P)$ 18.6 ($^2J(PCH)$ = 17 Hz)) (eq 2).[12] This latter conversion occurs

$$CH_2(PH(O)OH)_2 \xrightarrow{O_2} CH_2(PH(O)OH)(P(O)(OH)_2) \xrightarrow{O_2} CH_2(P(O)(OH)_2)_2 \quad (2)$$

only after aqueous solutions of $CH_2(PH(O)OH)_2$ have been boiled

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(7) Novikova, Z. S.; Prishchenko, A. A.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1977**, *47*, 775–781; *Chem. Abstr.* **1977**, *87*, 135606u. Kubiak, C. P.; Kullberg, M. L.; Lemke, F. R.; RaghuVeer, K. S.; King, C.; Roundhill, D. M., submitted for publication in *Inorg. Synth.*

(8) Frenz, B. A.; Okaya, Y. *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, Holland, 1982.

(9) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*; Universities of York, England, and Louvain, Belgium, 1978.

(10) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. Cromer, D. T. *Ibid.*; Table 2.3.1.

(11) Frank, A. W. In *Organic Phosphorus Compounds*; Kosolapoff, G. M.; Maier, L., Eds., Wiley: New York, 1972; Vol. 4, Chapter 10, p 263.

(12) Batley, M.; Redmond, J. W. *J. Magn. Reson.* **1982**, *49*, 172–174. Prishchenko, A. A.; Kolesnikova, G. G.; Novikova, Z. S.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1981**, *51*, 480–482; *Chem. Abstr.* **1981**, *95*, 62313z.

Table III. Bond Distances and Angles for $CH_2(PH(O)OH)_2$

	Distances (Å)		
P1-C	1.783 (1)	P2-O4	1.492 (1)
P1-O1	1.547 (1)	P2-H	1.277 (13)
P1-O2	1.488 (1)	C-H1	0.93 (2)
P1-H	1.300 (15)	C-H2	0.95 (2)
P2-C	1.791 (1)	O1-H	0.67 (3)
P2-O3	1.542 (1)	O2-H	0.56 (2)
	Angles (deg)		
P1-C-P2	116.82 (7)	O3-P2-O4	115.46 (7)
O1-P1-O2	115.78 (6)	O3-P2-C	104.96 (6)
O1-P1-C	105.13 (6)	O4-P1-C	112.56 (6)
O2-P1-C	111.21 (6)	P1-O1-H	109 (2)
P2-O3-H	110 (2)		

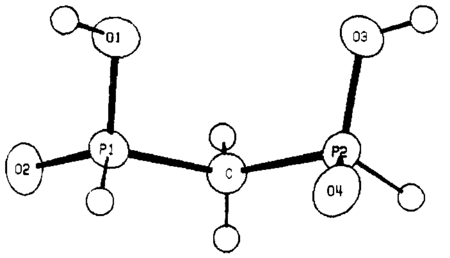

Figure 1. ORTEP view of the compound, $CH_2(PH(O)OH)_2$, showing the atom-labeling scheme.

in air for many hours. Basic solutions of $CH_2(PD(O)OD)_2$ in D_2O solvent convert over a period of several days to $CHD(PD(O)OD)_2$ and then to $CD_2(PD(O)OD)_2$ (eq 3).

$$CH_2(PD(O)OD)_2 \xrightarrow{D_2O} CHD(PD(O)OD)_2 \xrightarrow{D_2O} CD_2(PD(O)OD)_2 \quad (3)$$

Methylenebis(phosphinic acid) crystallizes in a monoclinic cell with space group $P2_1/n$ and $Z = 4$. The crystal structure is composed of intermolecularly hydrogen-bonded molecules of $CH_2(PH(O)OH)_2$. The molecular structure shows the methylenic group bonded to the PH(O)OH moieties at distances of 1.783 (1) and 1.791 (1) Å for P1-C and P2-C, respectively, and with a P1-C-P2 angle of 116.82 (7)°. The long P—OH (P1-O1, P2-O3) and short P=O (P1-O2, P2-O4) distances are 1.547 (1), 1.542 (1), 1.488 (1), and 1.492 (1) Å, respectively. We find the P-H distances to be 1.300 (15) Å (P1-H) and 1.277 (13) Å (P2-H). The intermolecular separation between oxygens at the ends is 2.508 (2) Å (O1-H-O4) and 2.513 (2) Å (O2-H-O3), each separation being close enough to involve hydrogen bonding.[13] The refined O-H distances are very short, but this may be a consequence of the data set size. A view of the compound is shown in Figure 1, and distances and angles are given in Table III. To our knowledge this is the first full structural characterization of a phosphinic acid, although the detailed X-ray structure of methylenebis(phosphonic acid) has been published.[14]

By comparison the structure of methylenebis(phosphonic acid) shows closely analogous bonding distances, none of which are significantly different than those we find for methylenebis(phosphinic acid). For $CH_2(P(O)(OH)_2)_2$ the P-C distance is 1.793 (3) [2] Å and the PCP angle is 117.2 (1)°. The former is statistically identical with our values, and the latter angle is within 2 or 3 standard deviations of ours in $CH_2(PH(O)OH)_2$. The P—O and P=O bond distances are equally comparable.

Preliminary studies verify that methylenebis(phosphinic acid) forms luminescent platinum complexes, and the coordination chemistry of this new compound with the platinum group of elements is currently being investigated.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. $CH_2(PH(O)OH)_2$, 81050-37-5; $CH_2(PCl_2)_2$, 28240-68-8; $CH_2(PH(O)OD)(PD(O)OD)$, 100859-24-3; $CH_2(PH(O)OH)(P(O)(OH)_2)$, 80987-09-3; $CH_2(PH(O)(OH)_2)_2$, 1984-15-2.

Supplementary Material Available: Listings of anisotropic thermal parameters, observed and calculated structure factor amplitudes, and selected torsion angles (10 pages). Ordering information is given on any current masthead page.

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(13) Roundhill, D. M.; Sperline, R. P.; Beaulieu, W. B. *Coord. Chem. Rev.* **1978**, *26*, 263–279. Walther, B. *Coord. Chem. Rev.* **1984**, *60*, 67–105.

(14) Peterson, S. W.; Gebert, E.; Reis, A. H., Jr.; Druyan, M. E.; Mason, G. W.; Peppard, D. F. *J. Phys. Chem.* **1977**, *81*, 466–471.

Additions and Corrections

1984, Volume 23

Robert Bender, Pierre Braunstein,* Jean-Marc Jud, and Yves Dusausoy: Comparison of Two Strategies toward the Synthesis of Platinum Mixed-Metal Clusters. Reactivity of Linear M–Pt–M and Mn–Pt–Mn Complexes. X-ray Crystal Structures of $Pt_2M_2(\eta\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2(\mu\text{-}CO)_4(PEt_3)_2$ with M = Cr, Mo, and W.

Page 4491. In footnote 25, giving the preliminary X-ray structural data of *trans*-$Pt(H)Cl(PPh_3)_2$, the complete crystal data should read as follows: $C_{36}H_{31}ClP_2Pt$, triclinic, space group $P\bar{1}$; $a = 18.38$ (1), $b = 9.65$ (1), $c = 20.60$ (1) Å; $\alpha = 91.15$ (3), $\beta = 96.52$ (4), $\gamma = 99.54$ (6)°; $Z = 2$.—Pierre Braunstein

1985, Volume 24

Diane L. Packett, Craig M. Jensen, Robert L. Cowan, Charles E. Strouse,* and William C. Trogler*: Syntheses, Structures, and Mechanism of Formation of *trans*-Chlorohydrobis(trimethylphosphine)platinum(II) and *trans*-Dihydrobis(trimethylphosphine)platinum(II). Energetics of Cis–Trans Isomerization.

Page 3581. Studies of IR spectra in several solvents show that the 1715-cm^{-1} IR absorption we attributed to *cis*- and *trans*-$PtH_2(PMe_3)_2$ results from the asymmetric Pt–H stretch of the trans isomer. The cis isomer exhibits broad overlapping absorptions at 2030 and 1985 cm^{-1} attributable to the IR-allowed symmetric and asymmetric Pt–H stretching vibrations, respectively.—Diane L. Packett and William C. Trogler