

latter compound (Figure 1) shows clearly that the rhodium atoms of this molecule are inequivalent; the resonances are manifested as a pair of doublets centered at $\delta = \text{ca. } 7644$ and 4322 ($14.3 \times 10^{22} \text{ cm}^{-3}$) splitting of each doublet is ca. 35 Hz.

The large differences between these ^{103}Rh resonance positions is quite remarkable and is a dramatic illustration of the sensitivity of this measurement to changes in the immediate environment of this nucleus. In this case, this environment consists of $\text{Rh}(\text{N}_2\text{O}_2\text{Rh})$ (in $[\text{Rh}_2(\text{mhp})_4]$) and $\text{Rh}(\text{N}_3\text{ORh})$ and $\text{Rh}(\text{NO}_3\text{Rh})$ (in $[(\text{Rh}_2(\text{mhp})_4)_2]$) and it is notable that the average of the chemical shifts of these last two nuclei (5984 ppm) is close to the chemical shift of the first (5745 ppm).

The splitting of the ^{103}Rh resonances of $[(\text{Rh}_2(\text{mhp})_4)_2]$ into doublets is attributed to $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ coupling, primarily as a result of a direct interaction via a metal-metal single bond. The value of $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ ($K_{XY}(2\pi/\hbar\gamma_X\gamma_Y)J_{XY}$)¹⁹ of 35 Hz ($29.4 \times 10^{22} \text{ cm}^{-3}$) is the largest so far observed directly. Lawson and Shapley²⁰ have reported $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ values of 4.2 Hz ($3.5 \times 10^{22} \text{ cm}^{-3}$) and 4.4 Hz ($3.7 \times 10^{22} \text{ cm}^{-3}$) for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_3]$ and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{NO})_2]$, respectively, and Caddy et al.²¹ have indicated that $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ (K) is 17 Hz alone or for $[\text{Rh}_2(\text{C}_2\text{H}_5)(\text{C}_2\text{HMe}_2)(\eta^5\text{-C}_9\text{H}_7)_2]$. However, Mague and Sanger have claimed²² $^1J(^{103}\text{Rh}, ^{103}\text{Rh})$ (K) values of 128 (± 25) Hz ($107.6 (\pm 21.0) \times 10^{22} \text{ cm}^{-3}$) and 167 (± 15) Hz ($140.3 (\pm 12.6) \times 10^{22} \text{ cm}^{-3}$) from the ^{31}P NMR spectra of the "A-frame" complexes $[\text{Rh}_2(\text{CO})_3\text{Cl}(\text{dpm})_2]-[\text{BPh}_4]$ ($\text{dpm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) and $[\text{Rh}_2\text{Cl}_2(\text{SO}_2)(\text{dpm})_2]-[\text{BPh}_4]$, respectively. The magnitudes of these latter two coupling constants seem surprisingly large, in view of those observed directly, especially for $[(\text{Rh}_2(\text{mhp})_4)_2]$.

Previous discussions^{19,20,23} have suggested that the dominant contribution to a $^1K_{XY}$ value is the Fermi contact term, which is predicted to be fairly large and positive for an appreciable s-orbital involvement in the X-Y bond. This view, with respect to the $^1K_{\text{RhRh}}$ value for $[(\text{Rh}_2(\text{mhp})_4)_2]$, appears to be reasonably consistent with the current theoretical interpretations⁹⁻¹¹ of $\text{Rh}^{\text{II}}-\text{Rh}^{\text{II}}$ interactions. There is now general agreement that the 14 electrons of a Rh_2^{4+} center fill the σ , π , δ , δ^* , and π^* orbitals of the metal-metal framework; the latest calculations¹¹ favor the orbital sequence $\pi^4\delta^2\pi^4\delta^*\sigma^2$, for a $[\text{Rh}_2(\text{O}_2\text{CR})_4]$ complex alone or with axially coordinated H_2O molecules, with a 5s contribution to the Rh-Rh σ orbital of ca. 0.25.

The results of the study clearly demonstrate that ^{103}Rh NMR spectroscopy is potentially a very useful technique for the study of complexes based on the Rh_2^{4+} center, and further studies are in progress.

Acknowledgment. We thank the SERC and The Cancer Research Campaign for financial support.

Registry No. $[\text{Rh}_2(\text{mhp})_4]$, 75310-08-6; $[(\text{Rh}_2(\text{mhp})_4)_2]$, 89655-97-0.

- (19) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1969**, *51*, 2790.
 (20) Lawson, R. J.; Shapley, J. R. *Inorg. Chem.* **1978**, *17*, 2963.
 (21) Caddy, P.; Green, M.; Smart, L. E.; White, N. *J. Chem. Soc., Chem. Commun.* **1978**, 839.
 (22) Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060.
 (23) Pople, J. A.; Santry, D. P. *Mol. Phys.* **1964**, *8*, 1.

Department of Chemistry
 Manchester University
 Manchester M13 9PL, U.K.

C. David Garner*
 Madeleine Berry

Department of Chemistry
 Sheffield University
 Sheffield S3 7HF, U.K.

Brian E. Mann

Synthesis and Characterization of a Technetium Phosphite Complex: Hexakis(trimethyl phosphite)technetium(I) Tetraphenylborate

Sir:

Binary zerovalent or low-valent transition-metal phosphite complexes are interesting because of their analogy to transition-metal carbonyls and their applications in catalysis. Well-characterized zerovalent complexes include $\text{M}[\text{P}(\text{OCH}_3)_3]_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$),¹⁻⁵ $\text{Re}_2[\text{P}(\text{OR}_3)_{10}]$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$),^{2,6,7} $\text{M}[\text{P}(\text{OR}_3)_5]$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}, \text{R} = \text{CH}_3$; $\text{M} = \text{Fe}, \text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{R}_3 = (\text{CH}_2)_3\text{CC}_2\text{H}_5$),⁸⁻¹³ $\text{M}_2[\text{P}(\text{OR}_3)_8]$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}, \text{R} = \text{aryl}$; $\text{M} = \text{Co}, \text{R} = \text{CH}_3, \text{C}_2\text{H}_5$),¹⁴⁻¹⁸ $\text{M}[\text{P}(\text{OR}_3)_4]$ ($\text{M} = \text{Co}, \text{Ni}, \text{Pd}, \text{Pt}, \text{R} = \text{CH}_3$; $\text{M} = \text{Co}, \text{R} = i\text{-C}_3\text{H}_7$; $\text{M} = \text{Ni}, \text{Pt}, \text{R} = \text{aryl}$); and numerous others where $\text{M} = \text{Ni}$),^{14,16,19-27} and $\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$.²⁸ Among the low-valent complexes are $\text{Fe}[\text{P}(\text{OCH}_3)_3]_{5,6}^{2+}$,^{9,11} $\text{M}[\text{P}(\text{OR}_3)_3]_5^+$ ($\text{M} = \text{Co}, \text{Rh}, \text{R} = \text{CH}_3$; $\text{M} = \text{Co}, \text{R} = \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7, \text{R}_3 = (\text{CH}_2)_3\text{CC}_2\text{H}_5$),^{8,10,14,16,29-32} $\text{Co}[\text{P}(\text{OR}_3)_6]^{3+}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7$),^{29,32} $\text{M}[\text{P}(\text{OR}_3)_5]^{2+}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{R} = \text{CH}_3$; $\text{M} = \text{Ni}, \text{R}_3 = (\text{CH}_2)_3\text{CC}_2\text{H}_5$),^{8,10,31,32} and $\text{M}[\text{P}(\text{OR}_3)_4]^+$ ($\text{M} = \text{Cu}, \text{Ag}, \text{R} = \text{CH}_3, \text{C}_2\text{H}_5$; $\text{M} = \text{Ag}, \text{R}_3 = (\text{CH}_2)_3\text{CC}_2\text{H}_5, (\text{CH}_3)_3(\text{CH}_2)_3$),³¹⁻³⁴ and the unusual anions $\text{Co}[\text{P}(\text{OR}_3)_3]_4^-$ ($\text{R} =$

- (1) Van-Catledge, F. A.; Ittel, S. D.; Tolman, C. A.; Jesson, J. P. *J. Chem. Soc., Chem. Commun.* **1980**, 254-255.
 (2) Choi, H. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 153-161.
 (3) Choi, H. W.; Gavin, R. M.; Muetterties, E. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1085.
 (4) Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Abdel-Meguid, S.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056-1059.
 (5) Mathieu, R.; Poilblanc, R. *Inorg. Chem.* **1972**, *11*, 1858-1861.
 (6) Choi, H. W.; Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1980**, *89*, 809-811.
 (7) Freni, M.; Romiti, P. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 167-170.
 (8) Jesson, J. P.; Cushing, M. A.; Ittel, S. D. *Inorg. Synth.* **1980**, *20*, 76-82.
 (9) Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966-6977.
 (10) Tolman, C. A.; Yarbrough, L. W., II; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 479-481.
 (11) Muetterties, E. L.; Rathke, J. W. *J. Chem. Soc., Chem. Commun.* **1974**, 850-851.
 (12) English, A. D.; Ittel, S. D.; Tolman, C. A.; Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 117-120.
 (13) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1982**, *1*, 453-459.
 (14) Muetterties, E. L.; Bleeke, J. R.; Yang, Z.-Y.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 2940-2942.
 (15) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920-7926.
 (16) Rakowski, M. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 739-743.
 (17) Robinson, S. D. *J. Chem. Soc., Chem. Commun.* **1968**, 521-522.
 (18) Mathieu, R.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1974**, 147.
 (19) Tolman, C. A.; Seidel, W. C.; Gasser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53-60.
 (20) Cundy, C. S.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 1647-1653.
 (21) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956-2965.
 (22) Hendrick, D. G.; McCarty, R. E.; King, R. W.; Verkade, J. G. *Inorg. Chem.* **1966**, *5*, 639-643.
 (23) Olechowski, J. R.; McAlister, C. G.; Clark, R. F. *Inorg. Chem.* **1965**, *4*, 246-247.
 (24) Empsall, H. D.; Green, M.; Shakshooski, S. K.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 3472-3476.
 (25) Meier, M.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1969**, *8*, 795-801.
 (26) Browning, J.; Empsall, H. D.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 381-387.
 (27) Malatesta, L.; Cariello, C. *J. Chem. Soc.* **1958**, 2323-2328.
 (28) Gasser, L. W.; Tolman, C. A. *Inorg. Chem.* **1970**, *9*, 2350-2353.
 (29) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 6978-6989.
 (30) Muetterties, E. L.; Watson, P. L. *J. Am. Chem. Soc.* **1976**, *98*, 4665-4667.
 (31) Coskran, K. J.; Bertrand, R. D.; Verkade, J. G. *J. Am. Chem. Soc.* **1967**, *89*, 4535-4537.
 (32) Coskran, K. L.; Huttemann, T. J.; Verkade, J. G. *Adv. Chem. Ser.* **1967**, No. 62, 590-603.

Received December 9, 1983

CH_3 , C_2H_5 , C_6H_5).^{14,15,35} Synthetic routes to these complexes usually start either with low-valent chlorides (which may be reduced by alkali-metal amalgams in the presence of phosphite) or with metal carbonyls that are activated thermally or photochemically to substitution by phosphite.

In this communication, we report the synthesis and characterization of the first binary technetium phosphite complex, $\text{Tc}[\text{P}(\text{OCH}_3)_3]_6^+$. This is the first ionic phosphite complex to be characterized from group 7B. The $\text{Re}[\text{P}(\text{OCH}_3)_3]_6^+$ species that was postulated has not yet been described.² In addition, we have prepared the complex by the direct reduction of NaTcO_4 with $\text{P}(\text{OCH}_3)_3$, an unprecedented reduction from M(VII) to M(I) in a single, fast, and simple reaction to give the phosphite complex. Finally, the title complex, a cationic technetium complex, is of interest in nuclear medicine, similar to other recently characterized cationic complexes.³⁶⁻³⁸

Synthesis of $\text{Tc}[\text{P}(\text{OCH}_3)_3]_6^+$ is readily accomplished in an inert atmosphere by adding excess $\text{P}(\text{OCH}_3)_3$ to a methanolic solution of NaTcO_4 (200:1 millimolar ratio), sealing the mixture in a pressure bottle (0.2 L), and heating at 100 °C for 0.5 h. Although the best yields are obtained by using freshly distilled $\text{P}(\text{OCH}_3)_3$ and dried methanol, substantial amounts of the complex form when reagents of lower purity are used. The reaction was not attempted in the presence of air or water because of the sensitivity of $\text{P}(\text{OCH}_3)_3$ to these substances. The ease with which the reduction from Tc(VII) to Tc(I) is accomplished is remarkable and demonstrates the powerful reductive action of $\text{P}(\text{OCH}_3)_3$ on oxo species. Reduction of sodium pertechnetate to the monovalent complex can be achieved in neat $\text{P}(\text{OCH}_3)_3$ and in tetrahydrofuran solutions of the ligand, demonstrating that $\text{P}(\text{OCH}_3)_3$ alone can be considered the reducing agent. Although methanol may also be involved in the reduction, its presence is not essential to the reaction. Other procedures leading to Tc(I) complexes either start with lower oxidation states, produce isolable intermediates, or use auxiliary reducing agents. For example, preparation of the $\text{Tc}(\text{CNR})_6^+$ complexes³⁸ uses TcO_4^- as starting material with dithionite as reducing agent, and in the dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) series,^{36,37} $\text{TcO}_2(\text{dmpe})_2^+$ and $\text{Tc}(\text{dmpe})_2\text{Cl}_2^+$ can be isolated as intermediates in the formation of $\text{Tc}(\text{dmpe})_3^+$, which appears only after prolonged reaction. Although the initial $\text{TcO}_4^-/\text{P}(\text{OCH}_3)_3$ solution is red and may contain a complex of the intermediate oxidation state, reduction to the Tc(I) compound proceeds even at room temperature.

Isolation of the $\text{Tc}[\text{P}(\text{OCH}_3)_3]_6^+$ cation is based on the low solubility of the tetraphenylborate salt in methanol. Thus, when an argon-saturated solution of $\text{NaB}(\text{C}_6\text{H}_5)_4$ in methanol (1 M) is added to the cooled reaction mixture, a white precipitate forms immediately. The precipitate can be collected by filtration using Schlenk techniques and recrystallized from methanol. Typical yields range from 50 to 75%, but a second and third crop of crystals can be grown by evaporation of the mother liquor, substantially increasing the yield. Depending on the rate at which the white-colorless crystals form, either needles (fast) or plates (slow) are obtained. The crystals are stable in air for at least 6 months. Elemental analyses on the crystalline material are consistent with the formulation $\text{Tc}[\text{P}(\text{OCH}_3)_3]_6\text{B}(\text{C}_6\text{H}_5)_4$.

Nuclear magnetic resonance spectra of $\text{Tc}[\text{P}(\text{OCH}_3)_3]_6^+$ were obtained for ^{99}Tc ($I = 9/2$) and ^{31}P ($I = 1/2$) in deuterated chloroform and methanol, respectively. The ^{99}Tc spectrum contains the expected septet centered at -422 ppm vs. TcO_4^- with a Tc-P coupling constant of 909 Hz. This coupling constant with technetium is much larger than those observed previously for oxygen, fluorine, or hydrogen³⁹ and implies a large Tc-P interaction. The ^{31}P spectrum contains a decet centered at -158.5 ppm vs. 85% H_3PO_4 with a P-Tc coupling constant of 909 Hz. This chemical shift is well within the range observed for other metal phosphite complexes.^{31,34} The ^{31}P spectrum clearly shows the nuclear Overhauser enhancement of the outermost peaks, whose intensity is noticeably larger than that of the eight inner peaks. The NMR spectra are readily interpreted as arising from an octahedral TcP_6 moiety containing six electronically equivalent phosphorus nuclei.

Mass spectra of $\text{Tc}[\text{P}(\text{OCH}_3)_3]_6\text{B}(\text{C}_6\text{H}_5)_4$ were obtained by fast atom bombardment mass spectrometry. In the positive-ion mode, the parent peak is at m/e 843 (calcd 843.4). Peaks at m/e 719, 595, and 471 correspond to loss of one, two, and three ligands from the parent ion. The peaks at m/e 719 and 595 are of approximately equal intensity and are the base peaks of the spectrum. Successive loss of CH_2 fragments is suggested by peaks occurring at m/e 829, 815, and 801 as well as m/e 705, 691, and 677. In the negative-ion mode, the parent peak is observed at m/e 319 (calcd 319.2).

Infrared spectra of $\text{Tc}[\text{P}(\text{OCH}_3)_3]_6\text{B}(\text{C}_6\text{H}_5)_4$ were taken from a pressed KBr pellet. The vibrational frequencies due to the P-O bonds shifted to higher energy in the complex (1011 to 1048 and 726 to 762 cm^{-1}), indicating that the $\text{P}(\text{OCH}_3)_3$ was coordinated to Tc. Bands due to $\text{B}(\text{C}_6\text{H}_5)_4^-$ were virtually unchanged from those of $\text{NaB}(\text{C}_6\text{H}_5)_4$, as expected for ionic tetraphenylborate.

In addition to the bands expected from $\text{P}(\text{OCH}_3)_3$ and $\text{B}(\text{C}_6\text{H}_5)_4^-$, an additional strong band that appeared at 538 cm^{-1} was tentatively assigned to a Tc-P vibration. Although a weak band does appear at 511 cm^{-1} in uncomplexed $\text{P}(\text{OCH}_3)_3$, the intensity of the band at 538 cm^{-1} suggests that it may include the Tc-P band since the relative intensities of all other $\text{P}(\text{OCH}_3)_3$ bands are unchanged from the uncomplexed ligand while this band greatly increases in intensity. However, in view of the fact that Tc-Cl stretching frequencies in $\text{Tc}(\text{diars})_2\text{Cl}_2^+$ (diars = 1,2-bis(diphenylarsino)ethane) occur near 330 cm^{-1} and those for $\text{Tc}(\text{dmpe})\text{Cl}_2^+$ are at nearly the same energy,⁴⁰ confirmation of the assignment of the Tc-P band must await infrared characterization of more members of this class of compounds.

(39) Franklin, K. J.; Lock, C. J. L.; Sayer, B. G.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 5303-5306.

(40) Glavan, K. A. Ph.D. Thesis, University of Cincinnati, 1982.

Diagnostic Product Group
Mallinckrodt, Inc.
St. Louis, Missouri 63134

Dennis W. Wester*
David H. White
Fred W. Miller
Richard T. Dean

Received February 14, 1984

- (33) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1983**, *22*, 592-596.
(34) Shupack, S. I.; Wagner, B. *J. Chem. Soc., Chem. Commun.* **1966**, 547-548.
(35) Muetterties, E. L.; Hirsekorn, F. *J. Chem. Soc., Chem. Commun.* **1973**, 684.
(36) Vanderheyden, J.-L.; Deutsch, E.; Libson, K.; Ketring, A. R. *J. Nucl. Med.* **1983**, *24*, P9.
(37) Subramanyam, V.; Linder, K. E.; Sammartano, M. C.; Pendleton, D. B.; Delano, M.; Liteplo, M.; Camin, L. L. *J. Nucl. Med.* **1983**, *24*, P9.
(38) Abrams, M. J.; Davison, A.; Jones, A. G.; Costello, C. E.; Pang, H. *Inorg. Chem.* **1983**, *22*, 2798-2800.

Isolation and Characterization of a Molybdenum-Containing Product in a Hydrazine-Forming Reaction¹

Sir:

The isolation of $\text{MoBr}_3(\text{triphos})$, where triphos = $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, from the ammonia-forming reaction of an-