Experimental Section

General Data.—Standard high-vacuum techniques[7] were used for the manipulation of all compounds. Starting materials and previously known reaction products were identified and checked for purity by vapor pressure, ir, and nmr. Hydrogen chloride and hydrogen iodide were obtained from the Matheson Co., but hydrogen bromide was prepared by the hydrolysis of PBr_3. Dimethylaminomethylfluorophosphine was prepared as described by Schmutzler.[8]

The ^1H, ^{19}F, and ^{31}P nmr spectra were determined with a Varian HR-100 operating at 100, 94.1, and 40.4 MHz, respectively. Mass spectra were determined at 70 eV with a Consolidated Electrodynamics Model 21-103B instrument. The infrared spectra were obtained on a Beckman IR-10 with an 87-mm gas cell equipped with KBr windows.

Preparation of CH_3PFX (X = Cl, Br).—The reaction was carried out in the gas phase in an apparatus consisting of two bulbs (2-l. capacity and 300-ml. capacity, respectively) separated by a stopcock. A similar apparatus has been previously described.[9] In a typical experiment for the preparation of CH_3PFCl, 4.32 mmol of HCl was condensed into the smaller bulb and the stopcock between the two bulbs closed. A 2.40-mmol sample of $CH_3PFN(CH_3)_2$ was condensed into the larger bulb. Both reactants were allowed to warm to 25°, and the stopcock between the two bulbs was opened, allowing the higher pressure HCl to expand into the larger bulb. An immediate reaction was observed by the formation of white clouds. The bulb was allowed to stand at 25° for 3 min and then the volatile products were condensed at −196°. Purification was effected by fractional condensation with traps held at −78, −111, and −196°. The −78° fraction contained 0.31 mmol of CH_3PCl_2 and a trace of $CH_3PFN(CH_3)_2$. The −196° trap contained 0.35 mmol of CH_3PF_2. The desired CH_3PFCl (1.42 mmol) was retained at −111°.

In a typical reaction for the preparation of CH_3PFBr a 5.75: 2.99 mmol ratio of $HBr:CH_3PF[N(CH_3)_2]$ was treated in the manner described above. The volatile products were separated by traps held at −63, −111, and −196°. The −63° fraction contained 0.51 mmol of CH_3PBr_2 and a small amount of CH_3PFBr. The −196° fraction contained 0.24 mmol of CH_3PF_2 and CH_3PF_3H. The −111° fraction contained 2.03 mmol of the desired CH_3PFBr.

Attempts to prepare CH_3PFI in the manner described for CH_3PFCl and CH_3PFBr yielded only CH_3PF_2, CH_3PF_4, some unreacted $CH_3PF[N(CH_3)_2]$, and intractable yellow-brown solids.

In all cases it is desirable to use a slight excess of $CH_3PF[N(CH_3)_2]$. An excess of HX promotes the disproportionation of CH_3PFX and typically results in the formation of larger amounts of CH_3PX_2 and CH_3PF_2 plus the formation of CH_3PF_3H.[5]

The vapor pressures (mm) observed for CH_3PFCl [−63.5° (7.2), −45.9° (25.6), −31.1° (61.8), −15.6° (145.5), 0.0° (290.6)] are described by the equation $\log p(\text{mm}) = -1451/T + 7.786$ which gives an extrapolated boiling point 22.6° and a Trouton constant of 22.45 cal/deg mol. The compound compound melts in the range −121.6 to −120.9°.

Vapor pressure data (mm) for CH_3PFBr below −31° are as follows: −45.5° (6.0), −35.8° (14.5), −31.2° (23.6). At higher temperatures disproportionation was too rapid to obobserve reliable pressures.

The mass spectrum of CH_3PFCl displayed the following fragmentation pattern (*m/e*, relative peak height, and assignment, respectively): 103, 0.6, $P^{35}Cl^{37}Cl^+$; 102, 16.0, $CH_3P^{37}ClF^+$; 101, 1.1, $CH_2P^{37}ClF^+$, $P^{35}Cl_2^+$; 100, 49.0, $CH_3P^{35}ClF^+$; 99, 0.8, $CH_2P^{35}ClF^+$; 87, 33.0, $P^{37}ClF^+$; 85, 100.0, $P^{35}ClF^+$; 81, 1.6, $CH_3P^{35}Cl^+$, $CHP^{37}Cl^+$; 80, 0.6, $CH_2P^{35}Cl^+$, $CP^{37}Cl^+$; 79, 3.2, $CHP^{35}Cl^+$; 78, 0.7, $CP^{35}Cl^+$; 69, 1.1, PF_2^+; 68, 0.8, $P^{37}Cl^+$; 66, 3.1, $P^{35}Cl^+$, $C^{35}ClF^+$; 65, 42.0, CH_3PF^+; 64, 9.2, CH_2PF^+; 63, 4.2, CHP^+; 62, 2.8, CPF^+; 51, 0.8, HPF^+; 50, 10.0, PF^+; 46, 1.1, CH_3P^+; 45, 29.0, CH_2P^+; 44, 13.0, CHP^+; 43, 3.3, CP^+; 37, 0.8, $^{37}Cl^+$; 36, 0.9, $H^{35}Cl^+$; 35, 2.7, $^{35}Cl^+$; 32, 0.8, PH^+; 31, 6.0, P^+.

The mass spectrum of CH_3PFBr gave the following pattern (*m/e*, relative peak height, and assignment, respectively): 146, 76.8, $CH_3P^{81}BrF^+$; 144, 77.6, $CH_3P^{79}BrF^+$; 131, 45.2, $P^{81}BrF^+$; 129, 45.6, $P^{79}BrF^+$; 125, 3.6, $CH_3P^{79}Br^+$, $CHP^{81}Br^+$; 123, 2.9, $CHP^{79}Br^+$; 112, 2.7, $P^{81}Br^+$; 110, 2.8, $P^{79}Br^+$; 107, 2.1, PF_4^+; 103, 2.6, $CH_3PF_3^+$; 102, 2.7, $CH_2PF_3^+$; 100, 8.2, CPF_3^+; 89, 5.5, PF_3H^+; 87, 5.0, ?; 85, 16.6, $CH_3PF_2H^+$; 84, 4.4, $CH_3PF_2^+$; 82, 2.0, $H^{81}Br^+$; 81, 6.8, $^{81}Br^+$; 80, 2.0, $H^{79}Br^+$; 79, 6.8, $^{79}Br^+$; 69, 12.4, PF_2^+; 66, 1.8, CH_3PFH^+; 65, 100.0, CH_3PF^+; 64, 16.9, CH_2PF^+; 63, 7.8, $CHPF^+$; 62, 4.4, CPF^+; 51, 1.7, PFH^+; 50, 22.1, PF^+; 46, 3.4, CH_3P^+; 45, 64.8, CH_2P^+; 44, 27.0, CHP^+; 43, 6.4, CP^+; 32, 5.0, PH^+; 31, 12.2, P^+.

Vapor densities in agreement with the mass spectral results were obtained by minimizing the time which CH_3PBr and CH_3PFCl remained liquid as they were vaporized to make the pressure–volume measurements

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The sponsorship of H. W. S. by the Civilian Institutions Program, Air Force Institute of Technology, is gratefully acknowledged.

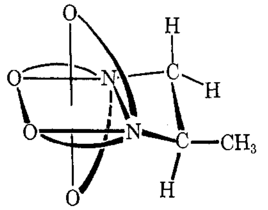
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

Evidence for an Axial Methyl Group in the Photolysis Product of (−)$_{5461}$-Rhodium(III) D-(−)-1,2-Propylenediaminetetraacetate[1]

BY GARY L. BLACKMER, JAMES L. SUDMEIER,
RICHARD N. THIBEDEAU, AND RICHARD M. WING*

Received March 17, 1971

Dwyer and Garvan, soon after demonstrating the stereoselectivity of the 1,2-propylenediaminetetraacetate (PDTA) ligand, observed that (−)$_{5461}$-Rh^{III}-D-(−)-PDTA, 1, suffered a loss of optical activity when exposed to ultraviolet radiation. The fully mutarotated sample was observed to regain its initial rotational strength completely upon storage in the dark for about 3 days.[2] This phenomenon, which is capable of many repetitions, was attributed to a photoaquation reaction in which a water molecule is substituted for a carboxylate ligand.



1

We have investigated the systems involving optically active Rh^{III}PDTA and Rh^{III}EDTA complexes by proton magnetic resonance (pmr) and circular dichroism (CD) in neutral solution (pH ∼6.5, the ligands being hexadentate[3]) and have reached a different conclusion as to the nature of the photolysis product.[4]

---

[7] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

[8] R. Schmutzler, *J. Chem. Soc.*, 5630 (1965).

[9] P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Amer. Chem. Soc.*, **89**, 2017 (1967).

[1] Supported by the National Science Foundation under Grant GP-19254 and by the National Institutes of Health under Grant R01-ES00477-04.

[2] F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **83**, 2610 (1961).

[3] B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, **7**, 2020 (1968).

[4] We have reproduced Dwyer and Garvan's results in all respects under these conditions. For (−)$_{5461}$-Rh^{III}-D-(−)-PDTA $[\alpha]_{5461}$ is −159.7°; after photolysis $[\alpha]_{5461}$ is −49.5°.

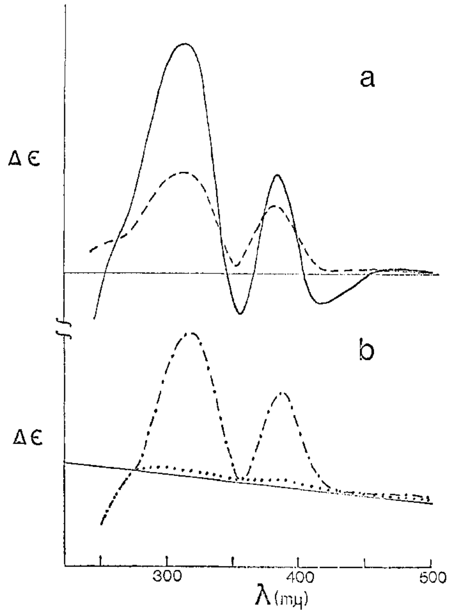


Figure 1.—(a) [(−)$_{5461}$-Rh^{III}-D-(−)-PDTA]$^-$ before photolysis and after dark recovery of 3 days in the dark (——) and immediately after photolysis (– – – –). (b) [(−)-Rh^{III}EDTA]$^-$ before photolysis (—·—·—·—), immediately after photolysis (——), and after 3 days in the dark (........).

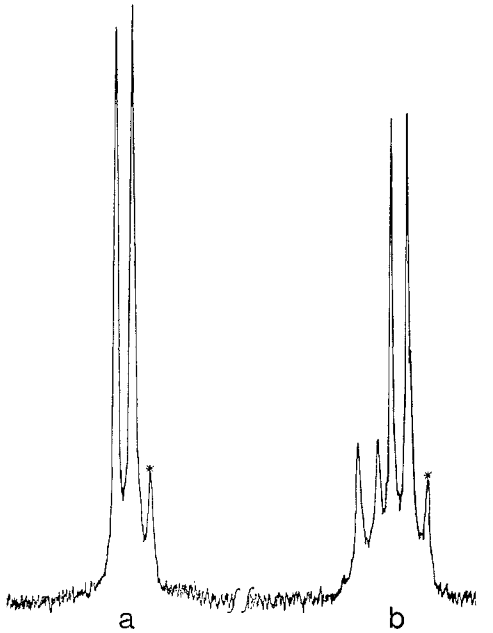
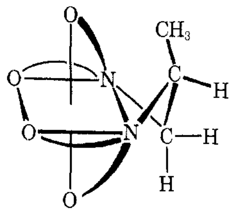


Figure 2.—(a) The 100-MHz pmr spectrum of the methyl resonances of [(−)$_{5461}$-Rh^{III}-D-(−)-PDTA]$^-$ before photolysis and after dark recovery for 3 days. (b) The 100-MHz pmr spectrum of the methyl resonances of [(−)$_{5461}$-Rh^{III}-D-(−)-PDTA)]$^-$ immediately after photolysis. The asterisk denotes an unassigned peak which is believed to be an impurity and shows no change during photolysis.

The CD spectrum of **1** before and immediately after photolysis by a low-pressure mercury arc[5] is shown in Figure 1a. There was no noticeable change in the absorption spectrum as a result of the photolysis. The emergence of a new methyl doublet and decreased intensity of the original methyl resonances (Figure 2) upon irradiation of the sample (relative areas 1:3, respectively) coincide with the loss of optical activity of the complex. No significant changes in the acetate portion[6] of the pmr spectrum of Rh(PDTA)$^-$ were observed upon photolysis of the sample indicating the hexadentate character of the ligand was retained.[7] Both the pmr and CD spectra revert back to those initially observed with a $t_{1/2}$ of 1 day at 23° when the sample is stored in the dark.

There are several molecular species which would account for the appearance of the new methyl group in the pmr spectrum of the photolysis product. Lack of significant change in the glycinate region of the pmr spectrum[8] tends to rule out a change in the denticity of the ligand. Lack of significant change in the ultraviolet–visible spectrum[9] tends to rule out a change in the coordination number of the rhodium ion.

We propose that the photolysis product is **2**, which



2

is the diastereomer of **1**. We would expect the visible region of the CD spectrum of **2** to approximate the spectrum of **1** but with opposite signs. When 75% of the CD spectrum of **1** is added to 25% of the expected CD spectrum of **2** (based on the 3:1 ratio between **1** and **2** observed by pmr), the resulting curve very closely approximates the observed CD spectrum of the photolyzed sample.

This photoracemization model was tested by irradiating a partially resolved[10] Rh(EDTA)$^-$ sample at pH 6.5.[11] In the case of Rh(EDTA)$^-$, racemized enantiomers would be of equal energy; thus no dark recovery of optical activity is expected.

The photoracemization model gives a ready explanation for the dark recovery of optical activity. Photolysis of **1** gives the diasteriomer **2**, which possesses an axial methyl group on the 1,2-propylenediamine backbone. This conformation, which has to our knowledge never been observed before, is less stable than the equatorial conformer by about 3 kcal/mol[12] (this energy

---

[5] Baush and Lomb SP-200, 200 W. The heat-producing infrared radiation was absorbed from the beam by passing it through a 1-l. flask of water. The flask served as a focusing lens. Photoequilibrium was achieved in ∼30 min for 0.2 *M* pmr samples and within 5 min for 10^{-3} *M* CD samples.

[6] In the study of Rh(PDTA)$^-$ the acetate AB pmr patterns were established by techniques outlined by J. L. Sudmeier, A. J. Senzel, and G. L. Blackmer, *Inorg. Chem.*, **10**, 90 (1971), and were assigned as a result of their close analogy to Co(PDTA)$^-$ as follows: AB-one (out-of-plane), H_a = 3.64 ppm, H_b = 4.25 ppm; AB-two (out-of-plane), H_a' = 4.00 ppm, H_b' = 4.13 ppm; AB-three (in-plane), H_c = 4.03 ppm, H_d = 3.82 ppm; AB-four (in-plane), H_c' = 3.96 ppm, H_d' = 3.84 ppm.

[7] Complete photodeuteration of all glycinate protons occurs within 3 hr of irradiation at a 0.2 *M* concentration.

[8] Pmr studies in this pH range (see B. B. Smith and R. H. Betts, *Inorg. Chem.*, **9**, 2585 (1970), and G. L. Blackmer and J. L. Sudmeier, *ibid.*, **10**, 2019 (1971)) show that when the EDTA ligand is forced to function as a pentadentate chelating agent (as a result of a monodentate ligand occupying one of the coordination positions of the metal ion), an upfield shift of an acetate AB pattern occurs (0.3–0.6 ppm) arising from the free (uncoordinated) glycinate ring protons.

[9] A shift in the position of the absorption maximum to longer wavelengths accompanies the protonation of a glycinate group of the D-(−)-PDTA ligand in a kinetically labile metal ion complex: K. P. Callahan, G. A. Ostrom, and R. M. Wing, *Inorg. Chem.*, **9**, 2605 (1970).

[10] J. I. Legg, *ibid.*, **7**, 1452 (1968).

[11] No change in the positions of the glycinate AB patterns from those cited in ref 3 occurred.

[12] (a) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959); (b) J. R. Gollogy and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).

difference being the reason for the stereospecificity of the PDTA ligand). Therefore a strong driving force exists for the return to conformation **1**. The rate of return, however, is very slow due to the kinetic inertness of the Rh(III) complexes.

At present, the details of the photochemical processes and the explanation of the photostationary state must await further investigation. It is interesting to note, however, that the photoequilibrium is established in less than 5 min in spite of the inertness of Rh(III) compounds.

Acknowledgment.—We thank Mr. Huai-Nan Cheng for experimental assistance.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
EASTERN ILLINOIS UNIVERSITY, CHARLESTON, ILLINOIS 61920

Tungsten Carbonyl Complexes Containing Positively Charged Phosphorus Ligands

BY R. L. KEITER* AND D. P. SHAH

Received March 29, 1971

Monoquaternized diamines as ligands have been investigated rather extensively by Quagliano and coworkers.[1] Few studies of monoquaternized diphosphines as ligands have been reported and most of these have been of complexes of transition metal halides which are usually insoluble and were studied in the solid state.[2-6] Only one carbonyl complex containing a monoquaternized diphosphine has been reported.[5]

Since CO stretching frequencies of metal carbonyls are especially sensitive to changes in electronic properties of coordinated ligands, small electronic changes in ligand-donating properties are detectable with ir spectroscopy. For example, it has been shown that the E modes of the carbonyl stretching frequencies of the complexes $(CO)_5WP(C_4H_9)_3$ and $(CO)_5WP(C_6H_5)_3$ are 1934 and 1942 cm^{-1}, respectively.[7] In this study a comparison of CO stretching frequencies and approximate force constants of $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ and $(CO)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$ with $[(CO)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2CH_2C_6H_5][PF_6^-]$ and $[(CO)_5WP(C_6H_5)_2CH_2P^+(C_6H_5)_2CH_3][I^-]$ is made.[8] These complexes are all sufficiently soluble in polar organic solvents to be studied in solution with ir and nmr spectroscopy.

Experimental Section

Proton nmr spectra were recorded with a Varian T-60 spectrometer. All nmr spectra were obtained from saturated deuteriochloroform solutions unless otherwise indicated. TMS was used as a reference in all measurements.

Infrared spectra in the carbonyl region were recorded with a Perkin-Elmer 337 infrared spectrometer. These spectra were expanded with an E.H. Sargent SR recorder and are considered to be accurate to ±2 cm^{-1}. Polystyrene was used as a frequency standard and chloroform was used as a solvent for each measurement.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Melting points were taken with an Arthur H. Thomas Unimelt apparatus and are reported uncorrected.

Preparation of Ligands. $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and $(C_6H_5)_2PCH_2P(C_6H_5)_2$.—These were prepared as previously described by Chatt and Hart.[9]

$[(C_6H_5)_2PCH_2CH_2P^+(C_6H_5)_2CH_2C_6H_5][Br^-]$.—This ligand was prepared by the method of Quagliano.[1]

$[(C_6H_5)_2PCH_2P^+(C_6H_5)_2CH_3][I^-]$.—To a solution of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (1.0 g, 0.0026 mol) in benzene (25 ml) was added CH_3I (0.37, 0.0026 mol). The product, a white solid, separated after several hours. The yield was essentially stoichiometric. The pmr spectrum consisted of, in addition to phenyl proton resonance, a doublet ($^2J_{P^+H}$ = 13.3 Hz) assigned to phosphonium–methyl proton coupling and a doublet ($^2J_{P^+H}$ = 15.0 Hz) assigned to phosphonium–methylene proton coupling centered at 2.73 and 4.10 ppm, respectively. The trivalent phosphorus–methylene proton coupling was too small to be resolved.

Preparation of Neutral Complexes. $(CO)_5WNH_2C_6H_5$.—This complex was prepared as previously described by Angelici and Malone.[10]

$(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ and $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2W(CO)_5$.—To a solution of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (3.0 g, 0.0075 mol) in benzene (100 ml) was added $(CO)_5WNH_2C_6H_5$ (1.0 g, 0.0023 mol). The solution was allowed to stand for 12 hr at room temperature and was taken to a thick oil with a rotary evaporator. The oil was dissolved in dichloromethane and an equal volume of methanol was added. The solution was cooled to 5° and white crystals slowly formed. These crystals, $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, were recrystallized from ethanol (yield 1.8 g). The pmr spectrum consisted of a complicated methylene region extending from 2.8 to 3.8 ppm and phenyl proton absorption. When $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (6.8 g, 0.017 mol) in 100 ml of benzene was treated with $(CO)_5WNH_2C_6H_5$ (6.0 g, 0.014 mol), only $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2W(CO)_5$ was recovered. The pmr spectrum consisted of a broad singlet at 2.30 ppm assigned to the methylene protons and the phenyl proton absorption.

$(CO)_5WP(C_6H_5)_2CH_2P(C_6H_5)_2$.—A solution of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (1.2 g, 0.003 mol) in acetone (25 ml) was mixed with a solution of $(CO)_5WNH_2C_6H_5$ (1.25 g) in benzene (50 ml). After 24 hr, the benzene–acetone solvent was removed with a rotary evaporator. The resulting oil was dissolved in equal volumes of dichloromethane and methanol. The solution was cooled to 5°, and white crystals slowly formed. Recrystallization from methanol gave the product (1.5 g). The pmr spectrum, in addition to the phenyl proton resonance, was found to be a doublet of doublets, centered at 3.29 ppm. The signal was first split by phosphorus coordinated to tungsten into a doublet ($^2J_{PH}$ = 8.60 Hz) and each member was further split into doublets ($^2J_{PH}$ = 2.40 Hz) by coupling with uncoordinated phosphorus.

Preparation of Positively Charged Complexes. $[(CO)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2CH_2C_6H_5][Br^-]$.—To a solution of $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$ (1.0, 0.0014 mol) in benzene (50 ml) was added $C_6H_5CH_2Br$ (0.237 g, 0.0014 mol). The white solid which separated after the solution had been stirred for several hours was washed with benzene to give 1.2 g of product. Attempts at recrystallization were unsuccessful. The same complex was also prepared in much lower yields by the direct interaction of $(CO)_5WNH_2C_6H_5$ and $[(C_6H_5)_2PCH_2CH_2P^+(C_6H_5)_2CH_2C_6H_5][Br^-]$. The pmr spectrum of the complex consisted of phenyl proton resonance, a broad methylene region extending from 1.8 to 3.2 ppm, and a doublet ($^2J_{PH}$ = 15.4 Hz), assigned to phosphorus–benzyl proton coupling, at 5.42 ppm.

---

[1] J. V. Quagliano, A. K. Banerjee, V. L. Goedken, and L. M. Vallarino, *J. Amer. Chem. Soc.*, **92**, 482 (1970).

[2] C. Ercolani, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chim. Acta*, **3**, 421 (1969).

[3] D. Berglund and D. W. Meek, *J. Amer. Chem. Soc.*, **90**, 518 (1968).

[4] D.Berglund and D. W. Meek, *Inorg. Chem.*, **8**, 2603 (1969).

[5] R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 71 (1970).

[6] R. C. Taylor and R. A. Kolodny, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, No. INOR 46.

[7] S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, **89**, 5573 (1967).

[8] The positive ligand complexes may be named (1-diphenylphosphino-2-benzyldiphenylphosphoniumethane)pentacarbonyltungsten(0) hexafluorophosphate and (1-diphenylphosphino-1-benzyldiphenylphosphoniummethane)pentacarbonyltungsten(0) iodide.

[9] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[10] R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).