

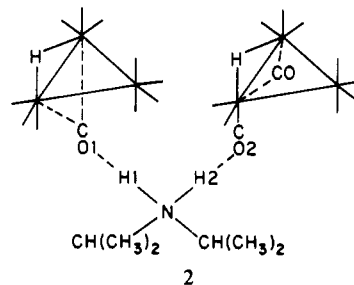
alcohol, and this might be the main reason that $\text{HFe}_3(\text{CO})_{11}^-$ is fully solvated in acetonitrile.

Interactions of Counteraction and $\text{HFe}_3(\text{CO})_{11}^-$ in the Solid State. Similar to the results observed in ether solution, the counteraction M^+ is also bound to the bridging CO in $\text{MHFe}_3(\text{CO})_{11}$ in the solid state as inferred from its relatively low bridging CO ν value compared to the ν value in acetonitrile (Table I). However, a noticeable difference in the trend of absorption frequency with the counteraction in the solid state and in solution was observed: the bridging CO ν value of the cesium salt at 1660 cm^{-1} is lower than the value of 1696 cm^{-1} for potassium and rubidium salts in the solid state, in contrast to the results in solution (Table I).

The IR absorption pattern of $\text{MHFe}_3(\text{CO})_{11}$ in solid state in the terminal carbonyl region is complicated and varies greatly with the counteraction, in contrast to the results observed in solutions. For the potassium and rubidium salts, a strong distinguished absorption occurs at 1906 cm^{-1} at the low end of the terminal CO region, which is absent for the corresponding cesium or PPN salt. The lowest terminal CO absorption of $\text{CsHFe}_3(\text{CO})_{11}$ occurs at 1930 cm^{-1} with a much weaker intensity than that of the 1906-cm^{-1} band described above. The higher bridging CO ν value and lower terminal CO ν value of $\text{KHFe}_3(\text{CO})_{11}$ and $\text{RbHFe}_3(\text{CO})_{11}$ relative to the cesium salt may be explained by the presence of a significant counteraction-terminal CO interaction, in addition to the known bonding between the cation and the bridging CO group in the potassium and rubidium salts. As a well-known phenomenon, the cation-terminal CO interaction would lead to an electron flow from the iron atoms to the π^* orbitals of the bonded t-CO group and a lower stretching frequency for the CO group. However, the interaction reduces the acidity of the cation, weakens the bonding between the cation and the bridging CO group, and consequently results in a higher bridging CO ν value for $\text{KHFe}_3(\text{CO})_{11}$ or $\text{RbHFe}_3(\text{CO})_{11}$ relative to that of $\text{CsHFe}_3(\text{CO})_{10}$, which lacks such a cation-terminal CO interaction.

Further evidence in support of the interaction comes from the similarity of the IR spectra of $\text{MHFe}_3(\text{CO})_{11}$ ($\text{M} = \text{K},$

Rb) and $[(i\text{-Pr})_2\text{NH}_2]^+[\text{HFe}_3(\text{CO})_{11}]^-$ and the structure of the latter compound. The $[(i\text{-Pr})_2\text{NH}_2]^+$ salt also exhibits a strong IR absorption band at 1880 cm^{-1} at the low end of the terminal carbonyl region, and the results of X-ray structure determination of the compound indicate that the two hydrogens in the $[(i\text{-Pr})_2\text{NH}_2]^+$ group interact with the bridging CO in one $\text{HFe}_3(\text{CO})_{11}^-$ and one terminal CO in the other $\text{HFe}_3(\text{CO})_{11}^-$ (2).¹⁷ This hydrogen bonding between the terminal CO



and the $[(i\text{-Pr})_2\text{NH}_2]^+$ group apparently accounts for the low CO stretching frequency at 1880 cm^{-1} . The close resemblance of the IR spectra of $\text{MHFe}_3(\text{CO})_{11}$ ($\text{M} = \text{K}, \text{Rb}$) to that of the $[(i\text{-Pr})_2\text{NH}_2]^+$ salt leads us to the conclusion that a similar, but weaker, cation-terminal CO interaction also exists in the two alkali salts.

Acknowledgment. We thank the National Science Council of the Republic of China for the financial support of this work.

Registry No. $\text{KHFe}_3(\text{CO})_{11}$, 87145-35-5; $\text{LiHFe}_3(\text{CO})_{11}$, 87145-36-6; $\text{NaHFe}_3(\text{CO})_{11}$, 87145-37-7; $\text{CsHFe}_3(\text{CO})_{11}$, 38979-46-3; $\text{RbHFe}_3(\text{CO})_{11}$, 87155-47-3; $\text{Fe}(\text{CO})_5$, 13463-40-6; CO, 630-08-0; dibenzo-18-crown-6, 14187-32-7.

(17) Chen, C. K.; Cheng, C. H.; Hsu, C. S., results to be published. The bond distances are O1-H1 = 1.89 (1), O2-H2 = 2.09, N-O2 = 3.11, N-H1 = 1.078 (7), and N-H2 = 1.08 (1) Å. These values are in agreement with the formation of hydrogen bonds between O1 and H1 and between O2 and H2. See: Hamilton, W. C.; Ibers, J. C. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968.

Contribution from the Departments of Chemistry, Auburn University, Auburn, Alabama 36849, and University of Manchester Institute of Science and Technology, Manchester M60 1QD, United Kingdom

Trans Chelation in Transition-Metal Complexes: Synthesis and Characterization of Palladium(II) Complexes of Bis(diphenylarsino)alkanes

W. E. HILL,*† D. M. A. MINAHAN,† and C. A. McAULIFFE*†

Received May 17, 1982

A number of synthetic routes to the bis(tertiary arsines) $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{AsPh}_2$ ($n = 6-12, 16$) are described. These ligands form square-planar $\text{Pd}(\text{ligand})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CNS}$; $n = 6, 8, 10, 12, 16$) and $\text{Pd}(\text{ligand})\text{Cl}_2$ ($n = 7, 9, 11$) complexes, which have been characterized by elemental analyses, infrared and proton NMR spectroscopy, solid-state reflectance and solution visible/UV spectroscopy, and vapor-phase osmometry. Spectroscopic data indicate that the trans isomer is the only product when $n > 9$ and is the predominant one for $n < 9$. The molecular weights of the complexes are a function of the chelate chain length: polymeric species being preferred for short-chain ligands but monomeric units for the longer chain analogues ($n = 12, 16$). Evidence is given for the presence of both Pd-NCS and Pd-SCN linkages in the solid state and in solution for the thiocyanate derivatives. Factors affecting the formation of these trans-chelated complexes are discussed.

Introduction

The factors that govern trans chelation in square-planar transition-metal complexes have been a topic for much discussion in the recent literature,^{1,2} but no definitive postulate has yet appeared that explains the formation of cis and trans

bidentate chelate complexes. Since the isolation of the first trans-bonded bidentate complex by Issleib in 1961³ work on bidentate chelates with flexible backbones has indicated that the main factors that promote trans chelation are the presence

* Auburn University.

† University of Manchester Institute of Science and Technology.

(1) Hill, W. E.; McAuliffe, C. A.; Niven, I. E.; Parish, R. V. *Inorg. Chim. Acta* **1979**, *38*, 273.

(2) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972.

(3) Von Issleib, K.; Hohlfeld, G. *Z. Anorg. Allg. Chem.* **1961**, *3*, 312, 169.

Table I. Proton NMR Spectra of the Ligands Ph₂As(CH₂)_nAsPh₂ (n = 6–12, 16)

n (ligand)	δ (aromatic region) ^a	δ (aliphatic region) ^a	
6 (DAH)	7.49 (20)	2.32 (4)	1.65 (8)
7 (DAHP)	7.45 (20)	2.28 (4)	1.57 (10)
8 (DAO)	7.42 (20)	2.20 (4)	1.53 (12)
9 (DAN)	7.44 (20)	2.21 (4)	1.53 (14)
10 (DAD)	7.42 (20)	2.20 (4)	1.56 (16)
11 (DAY)	7.43 (20)	2.20 (4)	1.50 (18)
12 (DADOD)	7.46 (20)	2.21 (4)	1.52 (20)
16 (DAHd)	7.48 (20)	2.23 (4)	1.60 (28)

^a Measured relative to Me₄Si internal standard; relative intensities in parentheses.

of bulky substituent groups on the donor atoms and the length of the chelate backbone. Shaw proposed^{4,5} that "internal entropy" effects and chain length are related factors and that a chain length of less than five methylene units between the donor atoms would be too strained to allow trans coordination, while a chain length of greater than twelve methylene units would result in the formation of oligomeric trans-coordinated species.

Shaw's group has concentrated on synthesizing trans-chelated complexes using bulky tertiary butyl groups with flexible chelate backbones.^{2,6–8} Ligands of the type (*t*-Bu)₂P(CH₂)_nP(*t*-Bu)₂ (n = 8–10, 12) were used to synthesize trans-bonded complexes with palladium(II) and platinum(II). Mononuclear, dinuclear, and trinuclear complexes were isolated as were monomeric and dimeric species of iridium(I) and rhodium(I). Shaw was unable to synthesize the palladium(II) and platinum(II) complexes with the ligands Ph₂P(CH₂)₁₀PPh₂ and Me₂As(CH₂)₁₂AsMe₂ and proposed that the presence of bulky substituents on the ligand donor atom was a prerequisite for the formation of trans-chelated complexes. The isolation of monomeric trans-chelated species with flexible chelates of six to twelve methylene units in length appeared also to support the arguments based on "internal entropy" effects.⁵

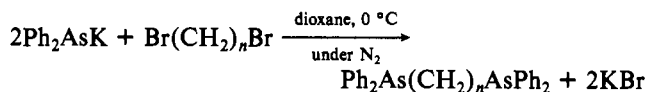
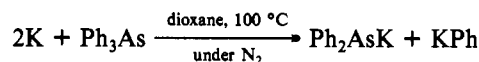
However, the synthesis of complexes of the type {PdX₂[Ph₂P(CH₂)_nPPh₂]}_m (n = 6, 8, 10, 12; m = 1, 2; X = Cl, Br, I, NCS),¹ {[PdCl₂[Me₂As(CH₂)₁₂AsMe₂]}₉, {MX₂[PhS(CH₂)₁₂SPh]} (M = Pd, Pt; X = Cl, Br),¹⁰ and {MCl₂[Me₂As(CH₂)₃S(CH₂)₃S(CH₂)₃AsMe₂]} (M = Pd, Pt) in solution in halocarbon solvents,^{11,12} all of which possess trans geometry, indicates that the presence of bulky substituent groups on the donor atom is *not* a prerequisite for trans chelation and that other factors such as (a) the nature of the donor atoms present in ligands, (b) the electronic effects of the groups attached to the donor atoms, (c) the nature of the central metal atom, (d) the nature of the complex precursor, and (e) the nature of the coordinated anion may all play significant roles in determining the coordination geometry of the complexes.

In this paper we report the syntheses and characterization of a wide range of palladium(II) complexes with bis(diphenylarsino)alkanes and discuss the factors that influence the

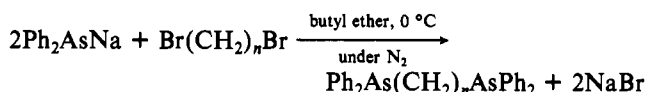
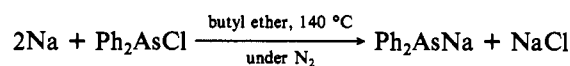
stereochemistry and product distribution in these complexes. The results obtained indicate that it is the nature of the central metal atom and the high trans effect of the ligand donor atoms and not the presence of bulky substituent groups on the donor atoms that are the primary factors that determine the geometry of the complexes.

Results and Discussion

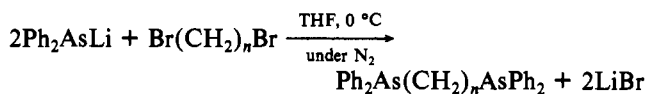
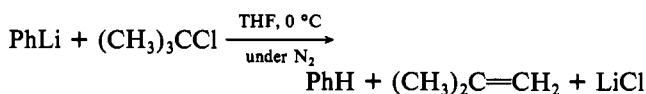
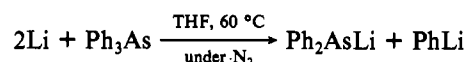
The synthesis of the bis(tertiary arsine) ligands are achieved by three separate routes. The first route was



The second route was



The final synthetic route involved



All these schemes give acceptable yields of the ligand, but the route employing triphenylarsine and lithium metal was that employed to synthesize the majority of the ligands since this experimental procedure is the least hazardous and involves the use of readily available starting materials.

The ligands were characterized by elemental analysis and proton and carbon-13 NMR spectroscopy. The analytical data for the ligands appear in the Experimental Section. In the cases where n = 7, 9, and 11 the ligands were obtained as hygroscopic oils that retained traces of solvent even under vacuum; however, these ligands gave the expected ¹H and ¹³C spectra and were employed as oils in the synthesis of the complexes.

The ¹³C NMR spectra of the ligands have been reported elsewhere.¹³ The proton NMR spectra (Table I) show three distinct resonances: a singlet at 7.4 ppm (Ph), a triplet at 2.3 ppm (As–CH₂), and a broad multiplet at 1.5 ppm (the remaining CH₂'s). The integrated intensities are in agreement with those expected for each ligand.

The chloro complexes were prepared by reacting palladium(II) chloride in dry ethanol with the ligand in dry toluene; 2,2-dimethoxypropane was added as a water scavenger, and the reaction mixture was stirred for 24 h. The solvent was then removed in vacuo and the solid extracted with dry toluene. After extraction, the solution was filtered and the complex was precipitated by adding a fivefold excess of ethanol. The precipitate was washed with dry diethyl ether and dried in vacuo. Bromo, iodo, and thiocyanato or isothiocyanato complexes were prepared by metathesis with a fivefold excess of lithium bromide, lithium iodide, or ammonium thiocyanate.

- (4) Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1973**, 947.
- (5) Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856.
- (6) Pryde, A.; Shaw, B. L.; Weeks, B. J. *J. Chem. Soc., Dalton Trans.* **1976**, 322.
- (7) Crocker, C.; Errington R. J.; McDonald, W. S.; Odell, K. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1979**, 498.
- (8) Crocker, C.; Errington R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 4373.
- (9) Levason, W.; McAuliffe, C. A.; Murray, S. G. *J. Organomet. Chem.* **1976**, *110*, C25.
- (10) Hartley, F. R.; Levason, W.; McAuliffe, C. A.; Murray, S. G.; Soutter, H. E. *J. Organomet. Chem.* **1978**, *159*, C25.
- (11) Levason, W.; McAuliffe, C. A.; Murray, S. G. *J. Organomet. Chem.* **1975**, *101*, C29.
- (12) Levason, W.; McAuliffe, C. A.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1976**, 2321.

- (13) Hill, W. E.; Minahan, D. M. A.; Taylor, J. G.; McAuliffe, C. A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 327.

Table II. Analytical Data for the Palladium(II)-Diarsine Complexes

complex	color	% C	% H	% X ^a
(DAH)PdCl ₂	yellow	50.1 (49.2) ^b	4.5 (4.8)	9.9 (9.0)
(DAH)PdCl ₂	yellow	50.8 (50.1)	4.6 (4.3)	9.7 (9.2)
(DAO)PdCl ₂	yellow	51.4 (50.6)	4.8 (4.5)	9.5 (9.2)
(DAN)PdCl ₂	yellow	52.0 (52.8)	5.0 (5.1)	9.3 (10.0)
(DAD)PdCl ₂	yellow	52.7 (53.2)	5.2 (5.1)	9.2 (8.6)
(DAU)PdCl ₂	yellow	53.2 (53.2)	5.3 (4.8)	9.0 (8.8)
(DADOD)PdCl ₂	yellow	53.8 (52.6)	5.5 (5.7)	8.8 (8.1)
(DAH)PdBr ₂	yellow/brown	44.5 (44.7)	4.0 (3.9)	19.8 (20.0)
(DAD)PdBr ₂	yellow/brown	45.9 (45.6)	4.3 (4.5)	19.1 (19.6)
(DAD)PdBr ₂	yellow/brown	47.2 (48.4)	4.6 (4.9)	18.5 (17.7)
(DADOD)PdBr ₂	yellow/brown	48.4 (48.1)	4.9 (4.9)	17.9 (17.4)
(DAH)PdI ₂	brown	39.9 (40.3)	3.5 (4.1)	28.1 (28.6)
(DAO)PdI ₂	brown	41.3 (41.0)	3.9 (3.8)	27.3 (27.0)
(DAD)PdI ₂	brown	42.6 (42.8)	4.2 (4.4)	26.5 (26.8)
(DADOD)PdI ₂	brown	43.6 (43.8)	4.4 (4.2)	25.7 (26.2)
(DAH)Pd(CNS) ₂	orange	50.2 (50.1)	4.2 (4.2)	3.6 (3.7)
(DAO)Pd(CNS) ₂	orange	51.5 (50.3)	4.5 (4.3)	3.5 (4.4)
(DAD)Pd(CNS) ₂	orange	52.7 (51.8)	4.9 (4.8)	3.4 (3.5)
(DADOD)Pd(CNS) ₂	orange	53.7 (52.8)	5.2 (4.8)	3.3 (3.7)
(DAH)Pd(CNS) ₂	orange	55.7 (54.4)	5.7 (5.7)	3.1 (3.2)

^a X = I, N, Cl, Br. ^b Calcd (found).

Table III. Far-Infrared Spectra of the Chloro- and Bromopalladium(II) Complexes of the Diarsine Ligands

complex	$\nu(\text{M-X})$, ^a cm ⁻¹	$\nu(\text{M-X})$, cm ⁻¹
(DAH)PdCl ₂	350	315, 285 ^b
(DAH)PdCl ₂	348	318, 288 ^b
(DAO)PdCl ₂	345	318, 286 ^b
(DAN)PdCl ₂	351	
(DAD)PdCl ₂	349	
(DAU)PdCl ₂	351	
(DADOD)PdCl ₂	351	
(DAH)PdBr ₂	248	220, 198 ^b
(DAO)PdBr ₂	248	218, 198 ^b
(DAD)PdBr ₂	251	
(DADOD)PdBr ₂	252	
(DAH)PdBr ₂	248	

^a Weak Pd-Br stretch. ^b Soluble component after extraction with C₆D₆. Nujol mull of solid obtained after the solvent was removed in vacuo.

Analytical data for the complexes appear in Table II.

The far-infrared spectra of the chloro and bromo complexes appear in Table III. All of the complexes exhibit one band (at 350 cm⁻¹ for the chloro derivatives and at 250 cm⁻¹ for the bromo derivatives) characteristic of trans halogen atoms.^{14,15} The band positions and intensities are in agreement with the literature reports.^{9,16,17} Palladium-iodide stretching vibrations occur below 180 cm⁻¹ and were not observed.

Metal-thiocyanato complexes have been extensively investigated in order to solve the interesting problem of whether the thiocyanato group is bound to the metal through the nitrogen atom (M-NCS), through the sulfur atom (M-SCN), or through both by means of a bridging structure (M-SCN-M).¹⁸⁻²¹ It appears that both electronic and stereochemical

Table IV. Infrared Spectra of the (Thiocyanato)palladium(II) Complexes of the Diarsine Ligands

	$\nu(\text{C-N})$, complex cm ⁻¹		$\nu(\text{C-N})$, complex cm ⁻¹
(DAH)Pd(SCN) ₂	2090 (m)	(DAD)Pd(SCN) ₂	2092 (m)
	2120 (m)		2118 (m)
	2160 (m)		2160 (w)
(DAD)Pd(SCN) ₂	2090 (m)	(DADOD)Pd(SCN) ₂	2089 (m)
	2120 (m)		2118 (m)
	2160 (w)		2160 (w)
(DAH)Pd(SCN) ₂	2085 (m)		
	2115 (w)		

explanations are important in determining the mode of bonding of the thiocyanato group, and attempts to explain the known facts in terms of only steric^{20,22} or only electronic^{23,24} factors are unlikely to be successful.²⁵

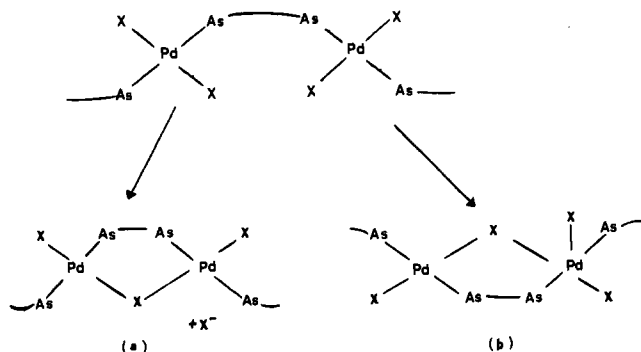
The solid-state infrared spectral data for the (thiocyanato)palladium(II) complexes of the diarsine ligands are given in Table IV. The C-S stretch and the NCS deformation modes are obscured by ligand bands, but the values for $\nu(\text{C-N})$ indicate the presence of both N- and S-bonded thiocyanato groups: the N-bonded group at 2090 cm⁻¹ and the S-bonded analogue at 2120 cm⁻¹. This is in agreement with reports for similar systems.^{26,27}

The compound [Pd(NCS)₂][Ph₂(CH₂)₂O(CH₂)₂O-(CH₂)₂PPh₂] gives two $\nu(\text{C-N})$ absorptions at 2090 and 2104 cm⁻¹ and is known by ³¹P NMR spectroscopy to be a mixture of N,N-, N,S-, and S,S-bonded isomers in solution,²⁸ and a

- (14) Nakamoto, K. "Infrared-red and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; p 203.
- (15) Adams, D. M. "Metal-Ligand and Related Vibrations"; St. Martin's Press: New York, 1968; p 319.
- (16) Coates, G. E.; Parkin, C. J. *Chem. Soc.* **1963**, 421.
- (17) Adams, D. M.; Chatt, J.; Gerratt, J.; Westland, A. D. *J. Chem. Soc.* **1964**, 734.
- (18) Burmeister, J. L. "The Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives"; Newmann, A. A., Ed.; Academic Press: London, 1975; pp 68-130.

- (19) Norbury, A. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 231.
- (20) Palenik, G. J.; Steffen, W. L.; Mathew, M.; Li, M.; Meek, D. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 973.
- (21) Dickinson, R. J.; Levason, W.; McAuliffe, C. A.; Parish, R. V. *Inorg. Chem.* **1976**, *15*, 2934.
- (22) Palenik, G. J.; Mathew, M.; Steffen, W. L.; Beran, G. J. *Am. Chem. Soc.* **1975**, *97*, 1059.
- (23) Norbury, A. H.; Sinha, I. I. *Q. Rev., Chem. Soc.* **1970**, *24*, 69.
- (24) Venanzi, L. M. *Chem. Ber.* **1968**, *4*, 162.
- (25) (a) Chow, K. K.; Levason, W.; McAuliffe, C. A. *Inorg. Chim. Acta* **1974**, *15*. (b) Nelson, J. H.; MacDougall, J. J.; Alcock, N. W.; Mathey, F. *Inorg. Chem.* **1982**, *21*, 1200.
- (26) Sabatini, A.; Bertini, I. *Inorg. Chem.* **1965**, *4*, 162.
- (27) MacDougall, J. J.; Verstyuyft, A. W.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1980**, *19*, 1036.
- (28) Falshaw, C. P.; King, T. J.; Hill, W. E.; Taylor, J. G.; Beagley, B.; McAuliffe, C. A.; Pritchard, R. G.; Tonge, D. M., submitted for publication.

Scheme I. Possible Mechanisms for the Production of Bridged Thiocyanate



similar situation probably exists for the diarsine complexes studied here. Interestingly a third component in the $\nu(\text{C-N})$ region in the solid state is observed at 2160 cm^{-1} in the region characteristic of bridging $-\text{NCS}-$ thiocyanato groups, and this component becomes steadily less intense as the chain length of the ligand increases and disappears altogether for $n = 16$. The band at 2160 cm^{-1} is absent in the solution spectra as would be expected since the polymeric material is insoluble.

It is reasonable to speculate on the nature of this polymeric material and why it is present, albeit in small amounts, in the complexes of the shorter chain ligands. In Scheme I we show the two possibilities that would allow us to see $\text{Pd}-\text{NCS}$, $\text{Pd}-\text{SCN}$, and $\text{Pd}-\text{NCS}-\text{Pd}$ linkages in the infrared spectrum. The starting material is square planar and contains trans arsines. Some of the terminal anions can bridge either (a) by displacing an anion and thus leaving the coordination number of the metal as 4 or (b) by bridging and increasing the coordination number of the metal to 5. We know, since the $\nu(\text{CN})$ band at 2160 cm^{-1} is weak, that the amount of bridging $-\text{NCS}-$ is small, but nevertheless, if route a occurs, then we should observe some uncoordinated NCS^- in the infrared spectrum. Since we do not, then we favor route b, which does involve the formation of some pentacoordinate palladium.²⁹ However, since the amount is small, then the electronic spectral bands of the pentacoordinate species are masked by the dominant planar species. We have evidence that for ligands with short chain lengths the polymeric species shown in Scheme I describes the structure. This type of structure probably allows the bridging process to occur, whereas the trans monomeric structure favors this process to a much less extent.

The proton NMR spectra of the complexes were examined, and the aromatic region of the spectra proved to be most informative. It has been noted by Keat³⁰ that the chemical shift separation, $\Delta\tau$, between ortho and meta/para protons in free triphenylphosphine increases (from $\Delta\tau = 0\text{ ppm}$ to $\Delta\tau = 0.33\text{ ppm}$) on changing the NMR solvent from CDCl_3 to C_6D_6 . More recently Moore and Robinson³¹ found that a similar phenomenon occurs in the proton NMR spectra of platinum metal complexes of triphenylphosphine, triphenylarsine, and triphenylstibine and this provides a convenient method for differentiation between cis and trans EPh_3 ligand pairs ($\text{E} = \text{P}, \text{As}, \text{Sb}$). The proton NMR spectra of the complexes studied here were examined to determine whether this technique could be extended to cover α,ω -bis(diphenylarsino)alkane complexes of palladium(II). The results are displayed in Table V, and from these data the following conclusion can be drawn. For the complexes with long chelate backbones ($n = 9-12, 16$), the soluble species in C_6D_6 show

Table V. Proton NMR Spectra of the Palladium(II) Complexes of the Diarsine Ligands in the Phenyl Region

complex	δ^a
(DAH)PdCl ₂	7.13
(DAH)PdCl ₂	7.12
(DAO)PdCl ₂	7.13
(DAN)PdCl ₂	7.00 (3), 7.81 (2)
(DAD)PdCl ₂	7.04 (3), 7.80 (2)
(DAU)PdCl ₂	7.01 (3), 7.78 (2)
(DADOD)PdCl ₂	6.98 (3), 7.78 (2)
(DAH)PdCl ₂	7.00 (3), 7.80 (2)
(DAH)PdBr ₂	7.10
(DAD)PdBr ₂	7.12
(DAD)PdBr ₂	7.07 (3), 7.79 (2)
(DADOD)PdBr ₂	6.99 (3), 7.81 (2)
(DAH)PdBr ₂	6.99 (3), 7.78 (2)
(DAH)PdI ₂	7.10
(DAO)PdI ₂	7.10
(DAD)PdI ₂	7.10 (3), 7.81 (2)
(DADOD)PdI ₂	7.13 (3), 7.81 (2)
(DAH)PdI ₂	7.12 (3), 7.79 (2)
(DAH)Pd(SCN) ₂	7.11
(DAO)Pd(SCN) ₂	7.14
(DAD)Pd(SCN) ₂	7.10 (3), 7.80 (2)
(DADOD)Pd(SCN) ₂	7.11 (3), 7.80 (2)
(DAH)Pd(SCN) ₂	6.99 (3), 7.79 (2)

^a Peaks measured relative to Me_4Si internal standard; relative intensities in parentheses.

chemical shift separations consistent with a trans arrangement for the bidentate ligands, confirming the results obtained from the far-infrared spectra of these complexes. For the complexes with short chelate backbones, ($n = 6-8$), the species soluble in C_6D_6 appear to possess a cis geometry. Examination of the far-infrared spectra of the soluble components also indicates the presence of cis species. However, these short-chain complexes are virtually insoluble in C_6D_6 due to their polymeric nature, and it appears, therefore, that these short-chain chelate complexes possess a small amount of a soluble cis component; the major component is still the trans isomer, which is insoluble in C_6D_6 or halocarbon solvents.

The proton spectra are not sensitive to a change in coordinated anion ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) in agreement with Moore and Robinson,³¹ suggesting that all of the compounds have the same basic structure.

The validity of the technique was confirmed by examining the proton NMR spectrum of the complex $\{\text{PdCl}_2[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{PPh}_2]\}$, which is known to possess cis geometry in the solid state and in solution.²⁸ The spectrum showed only one broad peak at 7.1 ppm in the aromatic region as expected for a cis complex. This spectrum is identical with those obtained for the diarsine complexes where $n = 6-8$. The trans species on the other hand ($n = 9-12, 16$) all show two distinct resonances at 7.8 and 7.0 ppm in a ratio of 2:3 with $\Delta\tau = 0.8\text{ ppm}$, as expected. The proton NMR spectra, therefore, confirm the assignments, made on the basis of the far-infrared spectra, and furthermore show the presence of a small quantity of a cis isomer present in solution when the alkane chain length is less than eight methylene units. This indicates that the trans species are most stable in the range $n = 9-16$ and are the dominant product when $n \leq 8$.

The electronic spectral data for the complexes are given in Table VI. The bands observed and the presence of a second band above 333 nm are in keeping with a square-planar geometry for the complexes both in the solid state and in solution.^{32,33} These bands move to lower energy in the order Cl

(29) Mair, G. A.; Powell, H. M.; Venanzi, L. M. *Proc. Chem. Soc., London* **1961**, 170.

(30) Keat, R. *Chem. Ind. (London)* **1968**, 1362.

(31) Moore, D. S.; Robinson, S. D. *Inorg. Chim. Acta* **1981**, *53*, 1171.

(32) Levason, W.; McAuliffe, C. A.; Murray, S. G. *Inorg. Chim. Acta* **1979**, *24*, 63.

(33) Levason, W.; McAuliffe, C. A. *J. Chem. Soc., Dalton Trans.* **1974**, 2238.

Table VI. Electronic Spectra of the Palladium(II)-Diarsine Complexes

complex	dichloromethane soln ^a	solid ^b
(DAH)PdCl ₂	29.4 (3100)	26.0
(DAHP)PdCl ₂	29.3 (3200)	26.1
(DAO)PdCl ₂	29.5 (3000)	26.0
(DAN)PdCl ₂	29.4 (3500)	26.2
(DAD)PdCl ₂	29.4 (3100)	26.0
(DAU)PdCl ₂	29.3 (3200)	26.1
(DADOD)PdCl ₂	29.4 (3200)	26.1
(DAHd)PdCl ₂	29.5 (3200)	26.0
(DAH)PdBr ₂	25.5 (3250)	24.5
(DAO)PdBr ₂	25.2 (3300)	24.6
(DAD)PdBr ₂	25.6 (3100)	24.6
(DADOD)PdBr ₂	25.8 (3200)	24.6
(DAHd)PdBr ₂	25.4 (3200)	24.6
(DAH)PdI ₂	21.1 (3500)	23.0
(DAO)PdI ₂	21.0 (3700)	23.2
(DAD)PdI ₂	21.1 (4100)	22.5
(DADOD)PdI ₂	21.1 (4000)	22.8
(DAHd)PdI ₂	21.4 (3600)	22.8
(DAH)Pd(SCN) ₂	26.7 (2300)	25.1
(DAO)Pd(SCN) ₂	26.7 (2400)	25.1
(DAD)Pd(SCN) ₂	26.8 (2000)	25.2
(DADOD)Pd(SCN) ₂	26.7 (2000)	25.3
(DAHd)Pd(SCN) ₂	26.7 (2300)	25.0

^a λ_{\max} in $\text{cm}^{-1} \times 10^3$; absorbance measured in $\text{L cm}^{-1} \text{mol}^{-1}$ in parentheses. ^b λ_{\max} in $\text{cm}^{-1} \times 10^3$; all peaks were broad.

> CNS > Br > I. The fact that the thiocyanato group is both N- and S-bonded in these complexes accounts for this unusual order: two N-bonded groups would produce the order NCS > Cl > Br > I, and two S-bonded groups would produce the order Cl > Br > SCN > I.³⁴

Molecular weight measurements in chloroform solution by vapor-phase osmometry indicate that when $n = 12$ and 16 , the complexes are monomeric, while for shorter chelate backbones the complexes are too insoluble for accurate measurement due to their polymeric nature. This parallels the work with long-chain bis(diphenylphosphino)alkane chelates with palladium(II).¹

Conclusions

While many square-planar platinum(II) complexes of the type PtX_2L_2 ($X = \text{halogen}$; $L = \text{tertiary phosphine}$) are known as both *cis* and *trans* isomers, the more labile palladium(II) complexes have usually been obtained as the *trans* form.³⁵⁻³⁷ The occurrence of *cis*-*trans* isomerization in bis(phosphine)-palladium(II) complexes is well established,³⁸ and in some cases either form reverts rapidly to an equilibrium mixture.^{39,40} However, in some cases only the *trans* form appears to exist either in the solid state or in solution.⁴¹ The preparation of the elusive *cis* derivatives has proved to be possible by photochemical means⁴²⁻⁴⁴ or by the employment of unusual com-

plex precursors.⁴⁵ The reaction of diphosphine ligands with palladium(II) salts would therefore be expected to give the *trans* isomer due to the lability of the groups coordinated to palladium(II) and the fact that, on coordination of the first phosphorus atom of the chelate, the atom *trans* to phosphorus would be labilized promoting substitution in the *trans* position, the only requirement being that the length of the chelate backbone be sufficient to allow the donor atoms to span the *trans* position. This is experimentally what is observed to happen for diphosphine ligands¹ and for the diarsine ligands examined here. *Trans* chelation is therefore effected due to the nature of the central metal atom and the high *trans* effect of the donor atoms present in the ligand and not due to the presence of bulky substituent groups on the donor atoms. The length of the chelate chain in the flexible bidentate ligands appears to dictate whether open-chain polynuclear species rather than large monomeric chelate rings are formed, and this can be explained in terms of ring strain⁴⁶ or entropy factors.² In the case of palladium(II), the nature of the complex precursor and the coordinated anion do not appear to play an appreciable role in determining the stereochemistry of the resulting complexes.

Experimental Section

The proton NMR spectra of the ligands were recorded on a Varian EM 390 spectrometer at a frequency of 90 MHz in deuteriochloroform with tetramethylsilane as the internal standard. The proton NMR spectra of the complexes were recorded on a Varian CFT-20 FT spectrometer at 80 MHz in deuteriochloroform with tetramethylsilane as the internal standard. The solid-state infrared spectra of the complexes were recorded on a Perkin-Elmer 580 spectrophotometer in Nujol mulls between polyethylene plates in the region 600-180 cm^{-1} . The solution spectra were recorded by using 1-mm path length polyethylene or potassium bromide cells in chloroform solution. The solution electronic spectra of the complexes in methylene chloride solution were recorded on a Cary 17 spectrophotometer using 1-cm path length cuvettes. The solid-state reflectance spectra were recorded on the same Cary 17 spectrophotometer fitted with the reflectance attachment. The base-line standard employed was magnesium carbonate. Molecular weights were determined in chloroform solution by vapor-phase osmometry. Elemental analyses were performed by the UMIST microanalytical service, the microanalytical service of Virginia Polytechnic Institute, Blacksburg, VA, and Galbraith Laboratories, Knoxville, TN.

Solvents were dried by the recommended literature routes;⁴⁷⁻⁴⁹ the ligands^{50,51} and complexes were prepared by standard procedures. Melting points for the $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{AsPh}_2$ ligands are 112-114 °C ($n = 6$), 104-106 °C ($n = 8$), 94-96 °C ($n = 10$), 86-88 °C ($n = 12$), and 66-68 °C, ($n = 16$). Elemental analyses [% calcd (% found)] are as follows for the ligands $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{AsPPh}_2$, listed as n (abbreviation): $n = 6$ (DAH): C, 66.4 (66.2); H, 5.9 (6.0). $n = 8$ (DAO): C, 67.4 (67.5); H, 6.3 (6.3). $n = 10$ (DAD): C, 68.2 (68.2); H, 6.7 (6.8). $n = 12$ (DADOD): C, 69.0 (69.0); H, 7.0 (7.6). $n = 16$ (DAHd): C, 70.4 (69.7); H, 7.6 (7.6).

Registry No. *cis*-(DAH)PdCl₂, 87206-81-3; *trans*-(DAH)PdCl₂, 87191-54-6; *cis*-(DAHP)PdCl₂, 87206-82-4; *trans*-(DAHP)PdCl₂, 87226-12-8; *cis*-(DAO)PdCl₂, 87206-83-5; *trans*-(DAO)PdCl₂, 87191-56-8; (DAN)PdCl₂, 87191-58-0; (DAD)PdCl₂, 87206-85-7; (DAY)PdCl₂, 87206-87-9; (DADOD)PdCl₂, 87191-43-3; (DAHd)PdCl₂, 87191-44-4; *cis*-(DAH)PdBr₂, 87191-51-3; *trans*-

- (34) Meek, D. W.; Nicpon, P. E.; Meek, V. I. *J. Am. Chem. Soc.* **1970**, *92*, 5351.
 (35) Booth, G. *Adv. Inorg. Chem. Radiochem.* **1964**, *1*, 6.
 (36) (a) McAuliffe, C. A. "Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands"; Macmillan: London, 1973. (b) McAuliffe, C. A.; Levason, W. "Phosphine, Arsine, and Stibine Complexes of the Transition Elements"; Elsevier: New York, 1979.
 (37) MacDougall, J. J.; Nelson, J. H.; Mathey, F.; Mayerle, J. *J. Inorg. Chem.* **1980**, *19*, 709. (b) MacDougall, J. J.; Mathey, F.; Nelson, J. H. *Ibid.* **1980**, *19*, 1460. (c) Knight, L. M.; Nelson, J. H. *Ibid.* **1977**, *16*, 1317.
 (38) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* **1971**, 3833.
 (39) Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 50.
 (40) Verstuyft, A. W.; Nelson, J. H. *Inorg. Chem.* **1975**, *14*, 1501 and references therein.
 (41) Grim, S. O.; Keiter, R. L. *Inorg. Chim. Acta* **1970**, *4*, 56.
 (42) Cusumano, M.; Guglieno, G.; Ricevuto, V.; Sostero, S.; Traverso, D.; Kemp, T. J. *J. Chem. Soc., Dalton Trans.* **1981**, 302.

- (43) Cusumano, M.; Guglieno, G.; Ricevuto, V.; Traverso, D.; Kemp, T. J. *J. Chem. Soc., Chem. Commun.* **1979**, 775.
 (44) Alcock, N. W.; Kemp, T. J.; Wimmer, F. L. *J. Chem. Soc., Dalton Trans.* **1981**, 635.
 (45) Uson, R.; Forries, J.; Espinet, P.; Martinez, F.; Tomas, M. *J. Chem. Soc., Dalton Trans.* **1981**, 463.
 (46) Hill, W. E.; Minahan, D. M. A.; Taylor, J. G.; McAuliffe, C. A.; *J. Am. Chem. Soc.* **1982**, *104*, 6001.
 (47) Burfield, D. R.; Gan, G. H.; Smithers, R. H. *J. Org. Chem.* **1977**, *42*, 3060.
 (48) Burfield, D. R.; Gan, G. H.; Smithers, R. H. *J. Appl. Chem. Biotechnol.* **1978**, *28*, 23.
 (49) Burfield, D. R.; Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 3966.
 (50) Tzschach, A.; Lange, W. *Chem. Ber.* **1962**, *95*, 1360.
 (51) Aguiar, A. M.; Archibald, T. G. *J. Org. Chem.* **1967**, *32*, 2627.

(DAH)PdBr₂, 87191-60-4; *cis*-(DAO)PdBr₂, 87191-52-4; *trans*-(DAO)PdBr₂, 87191-64-8; (DAD)PdBr₂, 87191-62-6; (DADOD)-PdBr₂, 87191-45-5; (DAHD)PdBr₂, 87191-46-6; (DAH)PdI₂, 87191-66-0; (DAO)PdI₂, 87191-68-2; (DAD)PdI₂, 87191-70-6; (DADOD)PdI₂, 87191-47-7; (DAHD)PdI₂, 87191-48-8; (DAH)Pd-(CNS)₂, 87191-72-8; (DAO)Pd(CNS)₂, 87191-74-0; (DAD)Pd-(CNS)₂, 87191-76-2; (DADOD)Pd(CNS)₂, 87191-49-9; (DAHD)-

Pd(CNS)₂, 87191-50-2; Ph₃As, 603-32-7; Ph₂AsCl, 712-48-1; Br(C-H₂)₆Br, 629-03-8; Br(CH₂)₇Br, 4549-31-9; Br(CH₂)₈Br, 4549-32-0; Br(CH₂)₉Br, 4549-33-1; Br(CH₂)₁₀Br, 4101-68-2; Br(CH₂)₁₁Br, 16696-65-4; Br(CH₂)₁₂Br, 3344-70-5; Br(CH₂)₁₆Br, 45223-18-5; DAH, 82195-43-5; DAHP, 82195-44-6; DAO, 82195-45-7; DAN, 82195-46-8; DAD, 82195-47-9; DAY, 82195-48-0; DADOD, 82195-49-1; DAHD, 82195-50-4.

Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Head-to-Head and Head-to-Tail Isomers of Binuclear Complexes of Platinum(I) and Palladium(I) Involving 2-(Diphenylphosphino)pyridine as a Bridging Ligand

JAMES P. FARR, FRED E. WOOD, and ALAN L. BALCH*

Received March 7, 1983

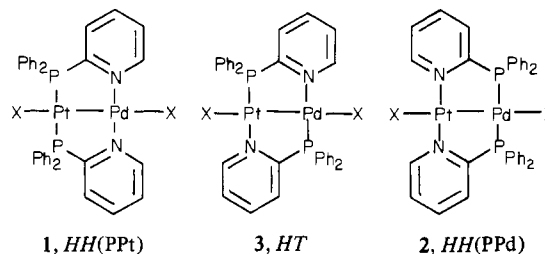
Reaction of Pt(Ph₂Ppy)₂Cl₂ (Ph₂Ppy is 2-(diphenylphosphino)pyridine) with Pd₂(dba)₃·CHCl₃ (dba is dibenzylideneacetone) or Pt(dba)₂ yields PtPd(μ-Ph₂Ppy)₂Cl₂ or Pt₂(μ-Ph₂Ppy)₂Cl₂, respectively. Extensive ³¹P{¹H} and ¹⁹⁵Pt{¹H} NMR studies show these exist as the head-to-tail (*HT*) isomers where the phosphorus atoms are bound to different metal atoms. Metathesis of Pt₂(μ-Ph₂Ppy)₂Cl₂ with sodium iodide yields the *HT* isomer of Pt₂(μ-Ph₂Ppy)₂I₂. Treatment of Pt(Ph₂Ppy)₂I₂ with Pd₂(dba)₃·CHCl₃ or Pt(dba)₂ yields PtPd(μ-Ph₂Ppy)₂I₂ or Pt₂(μ-Ph₂Ppy)₂I₂, respectively. These exist as the head-to-head (*HH*) isomers with both phosphines bound to the same platinum atom through phosphorus. The *HH* → *HT* isomerization of PtPd(μ-Ph₂Ppy)₂I₂ occurs on heating the *HH* complex in chloroform solution. In order to account for the selective preparation of *HT* isomers from Pt(Ph₂Ppy)₂Cl₂ and the formation of *HH* isomers from Pt(Ph₂Ppy)₂I₂, the solution composition of these two Pt(II) complexes has been examined. In solution, Pt(Ph₂Ppy)₂I₂ exists as a mixture of *cis* and *trans* isomers along with the salt [Pt(Ph₂Ppy)₂I]I while Pt(Ph₂Ppy)₂Cl₂ exists as the *cis* isomer and the salt [Pt(Ph₂Ppy)₂Cl]Cl. These salts contain one chelating and one monodentate phosphorus-bound Ph₂Ppy. An explanation for the selective formation of *HT* or *HH* isomers is offered.

Introduction

Binuclear, metal-metal-bonded compounds of Pt(I) and Pd(I) are readily prepared by a comproportionation reaction involving appropriate compounds of M(II) and M(0) (M = Pt or Pd).¹ For example, the unbridged dimer Pd₂(CNCH₃)₆²⁺ is formed by the reaction between methyl isocyanide, Pd^{II}(CNCH₃)₄²⁺ and Pd⁰(μ-dba)₃ (dba is dibenzylideneacetone, which coordinates as an olefin).² Likewise, the highly reactive dimer Pd₂(μ-dpm)₂Cl₂ (dpm is bis-(diphenylphosphino)methane) is reproducibly formed in good yield by the reaction between (PhCN)₂Pd^{II}Cl₂, Pd₂(μ-dba)₃, and dpm.³ Heterobinuclear dimers are also produced in this way. For example, mixing of Pt(dba)₂ with Pd(CNCH₃)₄²⁺ in the presence of methyl isocyanide yields PtPd(CNCH₃)₆²⁺ in high yield and in excellent purity.² This unbridged dimer retains its integrity under a variety of reaction conditions and establishes the robust character of the Pt-Pd bond.^{2,4} Similarly, PtPd(μ-dpm)₂Cl₂ has been formed from the reaction between Pd⁰(PPh₃)₄, (*t*-BuCN)₂PtCl₂, and dpm.⁵

In recent years we have been interested in constructing binuclear complexes using 2-(diphenylphosphino)pyridine (Ph₂Ppy) as a bridging ligand.^{6,10} We have reported that

Pd(Ph₂Ppy)₂Cl₂ reacts with Pd⁰(μ-dba)₃·CHCl₃ to form Pd₂(μ-Ph₂Ppy)₂Cl₂ and with Pt⁰(dba)₂ to form a mixture of Pd₂(μ-Ph₂Ppy)₂Cl₂ and PtPd(μ-Ph₂Ppy)₂Cl₂.¹¹ With an unsymmetrical bridging ligand such as Ph₂Ppy, it is possible to obtain stereoisomers that differ in the relative orientations of the bridging ligands. For a heterobinuclear species such as PtPd(μ-Ph₂Ppy)₂X₂, three isomers (the two head-to-head (*HH*) isomers **1** and **2** and the head-to-tail (*HT*) isomer **3**)



can exist while, for a homobinuclear species such as Pd₂(μ-Ph₂Ppy)₂Cl₂, only two isomers (one *HH* and the other *HT*) are possible. Preliminary evidence suggests that the PtPd(μ-Ph₂Ppy)₂Cl₂ formed by reaction 1 consisted exclusively of the Pd^{II}(Ph₂Ppy)₂Cl₂ + Pt⁰(dba)₂ → PtPd(μ-Ph₂Ppy)₂Cl₂ + Pd₂(μ-Ph₂Ppy)₂Cl₂ (1)

HT isomer.¹¹ These comproportionation reactions can be run

- Balch, A. L. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 651.
- Boehm, J. R.; Doonan, D. J.; Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 4845.
- (a) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099. (b) Benner, L. S.; Balch, A. L. *Inorg. Synth.* **1982**, *21*, 47.
- Boehm, J. R.; Balch, A. L. *Inorg. Chem.* **1977**, *16*, 778.
- Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 81.
- Farr, J. P.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 6654.
- Farr, J. P.; Olmstead, M. M.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 1182.

- Maisonnet, A.; Farr, J. P.; Olmstead, M. M.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 3961.
- Farr, J. P.; Olmstead, M. M.; Wood, F. E.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 792.
- Farr, J. P.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1983**, *22*, 1229.
- Maisonnet, A.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta* **1981**, *53*, L217.