cm^{-1} in $Cu(phen)_2ClO_4$. Our assignments follow those made previously for zinc(II) and mercury(II) complexes.[21] Changes in the infrared absorption spectra of iron complexes of phenanthroline and bipyridine have been cited as evidence in support of the postulation of enhanced π-bond formation,[20] but changes of similar magnitude are not observed for similar complexes with other metals. The changes in the infrared spectra are evidently not sufficient for the discussion of structures involving π bonding.

For the mixed complexes with triphenylphosphine and triphenylarsine, CuL_2CN, comparison of the infrared spectra of the complexes with those of the uncomplexed ligand clearly indicate coordination. Most of the vibrations associated with the aromatic rings are expected to occur in the same region irrespective of the substituent, but new lines occur at 1710 and 1715 cm^{-1} for $Cu(P(C_6H_5)_3)_2CN$ and $Cu(As(C_6H_5)_3)_2CN$, respectively. The prominent lines at 1090 and 1075 cm^{-1} in $P(C_6H_5)_3$ and $As(C_6H_5)_3$ also show a marked increase in intensity relative to the neighboring lines for the complexes $Cu(P(C_6H_5)_3)_2CN$ and $Cu(As(C_6H_5)_3)_2CN$. The lines which show the most prominent shifts on coordination are those associated with carbon–phosphorus and carbon–arsenic vibrations. In both cases the 690-cm^{-1} peak is shifted to 700 cm^{-1}, and the lines at 425 cm^{-1} ($P(C_6H_5)_3$) and 475 cm^{-1} ($As(C_6H_5)_3$) show an increase of 5–7 cm^{-1} on complex formation. The lines at 415 and 370 cm^{-1} ($P(C_6H_5)_3$) and 465 and 308 cm^{-1} ($As(C_6H_5)_3$) also show shifts of the same order. In view of the similarity of the spectra of triphenylphosphine and triphenylarsine, it is not surprising that the mixed complexes show only small changes.

Thus, the spectral evidence does not give direct evidence for either the presence or absence of significant metal–ligand bonding. Furthermore, the observation that the solid structures formed involve CN bridging of Cu atoms could indicate that the stability of these complexes is due solely to this stabilization and not to π bonding. However, the solution experiments must not be overlooked. It was shown that in methanol the ligands α,α'-bipyridine and *o*-phenanthroline stabilize Cu(I) more than Cu(II) while N-donor ligands having less π-bonding capability (α,α'-bipyridineamine, 2-aminoethanol, ethylenediamine,[8] and ammonia[8]) stabilize Cu(II) more than Cu(I). Apparently, π bonding does indeed play a role in stabilizing the mixed complexes of Cu(I). That this should be the case is consistent with the discussion of Kida concerning the importance of π bonding on mixed complex formation.[22] He notes, for example, that $Co(CN)_4(bipy)^-$ exists while $Co(CN)_4(en)^-$ is not known.

[21] K. Krishnan and R. A. Plane, unpublished work.

[22] S. Kida, *Bull. Chem. Soc. Japan*, **34**, 962 (1961).

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Metal Complexes of Unsaturated Tertiary Phosphines and Arsines. III. Group VI Metal–Olefin Complexes. An Unusual Metal-Catalyzed Olefin Isomerization[1,2]

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The preparation of a new chelating ligand, 2-allylphenyldiphenylphosphine (AP), and its application to the synthesis of the first monoolefin complexes of all three zerovalent group VI metals are described. The molecular formula of these complexes [$C_{21}H_{19}PM(CO)_4$; M = Cr, Mo, W] and their infrared spectra are consistent with coordination of both the phosphorus atom and a C=C bond to the group VI metal. However, nmr results show that the position of the C=C bond has been shifted upon coordination of the olefin to the metal and that the ligand in these complexes is the isomeric compound, 2-propenylphenyldiphenylphosphine. Moreover, by independent synthesis of both the *cis* and *trans* forms of this propenyl ligand and their corresponding group VI metal complexes it has been possible to show further that the coordinated olefin has the *cis* configuration. This isomerization of AP to the higher energy isomer of 2-propenylphenyldiphenylphosphine is discussed in light of previous transition metal catalyzed olefin isomerizations. The lowering in the C=C stretching frequency upon coordination of 2-*cis*-propenylphenyldiphenylphosphine to the zerovalent group VI metals is determined from infrared spectral measurements and is used to assess the degree of interaction between olefin and metal in these complexes.

Introduction

Recently, we reported the preparation of monoolefin complexes of all three zerovalent group VI metals.[3] The olefinic ligand used in this preparation was the new compound 2-allylphenyldiphenylphosphine (AP). At that time preliminary nmr results in-

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[1] Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] Part II: M. A. Bennett, G. J. Erskine, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, in press.

[3] M. A. Bennett, L. V. Interrante, and R. S. Nyholm, *Z. Naturforsch.*, **20b**, 633 (1965).

TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES

A. The Ligands and Intermediates in the Ligand Syntheses

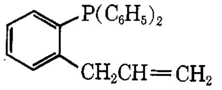
Compound	% C Calcd	% C Found	% H Calcd	% H Found	% halogen Calcd	% halogen Found	% P Calcd	% P Found
o-trans-$CH_3CH{=}CHC_6H_4Cl$	70.8	69.5	5.91	5.98	23.3	22.9		
o-cis-$CH_3CH{=}CHC_6H_4Cl$	70.8	71.2	5.91	5.86	23.3	23.3		
AP	83.5	83.3	6.33	6.29			10.3	10.2
trans-PP	83.5	83.1	6.33	6.64			10.3	10.2
cis-PP	83.5	83.3	6.33	6.26			10.3	10.1

B. The Metal Complexes

Compound	% C Calcd	% C Found	% H Calcd	% H Found	% Br Calcd	% Br Found	% P Calcd	% P Found	Mp, °C	Mol wt Calcd	Mol wt Found
(AP)$PtBr_2$	38.3	38.1	2.91	2.86	24.4	24.6	4.72	4.42	223–224 dec	657	669
(*cis*-PP)$PtBr_2$	38.3	38.3	2.91	2.88	24.4	24.5	4.72	4.96	265–267 dec	657	634
(*cis*-PP)$Cr(CO)_4$	64.4	64.4	4.10	4.07			6.66	6.75	189–190	466	455
(*cis*-PP)$Mo(CO)_4$	58.8	58.6	3.74	3.87			6.08	6.13	184–185 dec	510	516
(*cis*-PP)$W(CO)_4$	50.2	50.1	3.20	3.20			5.18	5.26	179–180 dec	598	610
(*trans*-PP)$Mo(CO)_4$	58.8	58.6	3.74	4.04			6.08	5.99	~130 dec	510	480

dicated that isomerization of the olefin accompanied the formation of these complexes.

We now present further details of the preparation of the group VI metal complexes and new evidence leading to the determination of the geometrical configuration of the coordinated olefin.



AP

Experimental Section

Starting Materials.—Hydrocarbon and ether solvents were distilled and dried over sodium. The norbornadiene complexes of zerovalent chromium and molybdenum were prepared as previously described[4] from the metal hexacarbonyls. Norbornadienetungsten tetracarbonyl [$C_7H_8W(CO)_4$] was prepared by slow addition (1 hr) under nitrogen of a solution of freshly distilled norbornadiene (15 ml) in 50 ml of heptane to a refluxing solution of $W(CO)_6$ (12.3 g) in 150 ml of heptane while irradiating with an ultraviolet light source. A low yield (1.2 g, 8.8%) of the diolefin complex (mp 92–95°) was obtained after recrystallization from hexane followed by fractional sublimation to remove $W(CO)_6$.[5] All other solvents and chemicals were of reagent grade quality and were used without further purification.

Measurements.—Infrared spectra were obtained in both deuteriochloroform and hexane solution as well as in the solid state as Nujol and hexachlorobutadiene mulls, using a Perkin-Elmer Model 421IR spectrophotometer for the region 3100–2500 cm^{-1} and a Model 237IR spectrophotometer between 2500 and 650 cm^{-1}. The nmr spectra were recorded on a Varian A60 nmr spectrophotometer in deuteriochloroform solution using *ca.* 1% tetramethylsilane (TMS) as an internal standard. Melting points were determined using a Büchi melting point apparatus and are corrected. Microanalyses and molecular weight measurements were performed by the microanalytical laboratories of the University of California at Berkeley and University College, London. The results of the analytical, molecular weight, and melting point measurements are summarized in Table I.

Preparation of Compounds. *o*-Chloroallylbenzene.—*o*-Chlorophenylmagnesium bromide was prepared by reaction of *o*-chlorobromobenzene (192 g, 1.00 mole) with magnesium (24.3 g, 1.00 g-atom) in 550 ml of ether.[6] Allyl bromide (121 g, 1.00 mole) in 150 ml of ether was then added during 2 hr fol owed by reflux for 1 hr more. The organic layer obtained upon hydrolysis of the reaction mixture with dilute hydrochloric acid was dried and the ether removed by distillation. The residue was distilled at 5 mm pressure to give 103 g (68%) of crude *o*-chloroallylbenzene (bp 60–70°) which was used in subsequent preparations without further purification.

2-Allylphenyldiphenylphosphine (AP).—This compound was prepared by a Grignard reaction carried out under an atmosphere of nitrogen in dry tetrahydrofuran (THF). The Grignard reagent of *o*-chloroallylbenzene (I) was prepared by slow addition (1.5 hr) of I (103 g, 0.675 mole) in 275 ml of THF to magnesium (16.4 g, 0.675 g-atom) in 150 ml of THF at 40–50° after initiating the reaction with 0.3 ml of methyl iodide and a small crystal of iodine. The reaction mixture was stirred at 40–50° for 1 hr after the addition and then heated to reflux for 6 hr. After cooling to room temperature, chlorodiphenylphosphine (148 g, 0.672 mole) in 150 ml of THF was added during 2 hr, followed by 1 hr of additional stirring and 1 hr of reflux. Dilute hydrochloric acid was then added and the organic layer separated by saturating the mixture with sodium chloride. The THF was removed by distillation leaving a viscous mass from which the 2-allylphenyldiphenylphosphine was extracted with *n*-pentane (700 ml in *ca.* 100-ml portions). Concentration of the pentane extracts to the point of saturation, followed by cooling to −78°, gave a white solid which was purified by vacuum sublimation; yield, 33.6 g (17.7%) of colorless white needles; mp 65–68°.

***o*-Chloropropenylbenzene.**—*o*-Chloroallylbenzene (95.5 g) was heated under reflux for 8 hr in a solution of 20 g of potassium hydroxide in 200 ml of *n*-amyl alcohol.[7] The reaction mixture was diluted with 300 ml of ether and extracted several times with 3 *M* hydrochloric acid and then with distilled water. The residue obtained after removing the ether was fractionally distilled at 5 mm pressure to give 76.7 g (80.3%) of *o*-chloropropenylbenzene (bp 60–72°; *ca.* 11.5:1 *trans*:*cis* by vapor phase chromatographic analysis).

***o*-Chloro-*cis*-propenylbenzene.**—This compound was prepared from the corresponding *trans* isomer by ultraviolet irradiation.[8] The *o*-chloropropenylbenzene from the preceding preparation (76.7 g) was separated into *ca.* 15-g portions, each of which was diluted with 500 ml of pentane and irradiated with ultraviolet light[9] under an atmosphere of nitrogen. The progress of the reaction was followed by vapor phase chromatography and

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[4] M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).

[5] This compound has recently been prepared by another method in better yield: R. B. King and A. Fronzaglia, *Chem. Commun.*, 547 (1965).

[6] M. Davis and F. G. Mann, *J. Chem. Soc.*, 3778 (1965).

[7] Tiffeneau, *Compt. Rend.*, **139**, 482 (1904).

[8] L. Crombie, *Quart. Rev.* (London), **6**, 106 (1952).

[9] The light source was a Hanovia L 450-w high-pressure mercury vapor lamp. A Corex filter was used to absorb light below 2800 A.

TABLE II

INFRARED DATA. ABSORPTION BANDS IN THE REGION 3100–650 CM^{-1} [a,b]

Assignment[c]	AP		(AP)PtBr$_2$		*trans*-PP		(*trans*-PP)Mo(CO)$_4$	
	Soln	Solid	Soln	Solid	Soln	Solid	Soln	Solid
Arom and olef C–H str		3073 w		3071 sh		~3069 sh		3072 sh
		3062 w		3059 w		3053 w		3063 w
		3015 vw		~3013 vw, b		3012 vw, b		
		3005 vw						
		2976 vw		~2986 sh				2979 w
Aliph C–H str						2958 vw		2949 vw
$C{\equiv}O$ str							2033 s	
							1942 vs	
							1923 vs	
							1912 vs	
$C{=}C$ str	1637 w		1492 sh		1642 vw, b		~1515 vw, b	
Arom ring str	1587 w		1587 w		1585 w		1585 w	
	~1563 vw		1570 vw				1570 sh	
	1478 w		1482 w		1474 w		1479 w	
Aliph C–H def	1464 w		1471 w		1456 w		1468 w	
	1435 m		1435 m		1437 m		1437 s	
Arom and olef C–H in-plane def	~1406 sh		1383 vw		1374 vw		1376 w	
							1362 sh	
	~1323 sh		1326 vw		1325 vw		1328 vw	
	1307 vw		1305 vw		1304 vw		1304 vw	
		1087 w		1092 m		1087 w		1094 m
		1027 w		1020 mw		1025 w		1035 mw, b
Arom and olef C–H out-of-plane def		908 m				959 m, b		929 w, b
				765 m				758 ms
		748 s		750 s		743 s, b		746 s
				711 m				
				700 ms				703 s
		696 s		688 s		694 s, b		693 s

[a] Only the major absorption bands below 1300 cm^{-1} are included. [b] vs, very strong; s, strong; ms, medium strong; m,

the irradiation terminated when the amount of *o*-chloro-*cis*-propenylbenzene in solution reached a maximum (*ca.* 6 hr; proportion of *trans*:*cis* at this point, *ca.* 1:1.7). The *o*-chloropropenylbenzene, enriched in the *cis* isomer, was recovered by distillation under reduced pressure (5 mm). The *cis* isomer was separated by means of preparative vapor phase chromatography using a Model A-700 automatic preparative gas chromatograph (Wilkins Instrument and Research, Inc.); yield, 11.6 g (15.1%) of *o*-chloro-*cis*-propenylbenzene.

2-*cis*-Propenylphenyldiphenylphosphine (*cis*-PP).—This compound was prepared according to the procedure described for 2-allylphenyldiphenylphosphine. *o*-Chloro-*cis*-propenylbenzene (11.58 g, 7.59 × 10^{-2} mole) and equimolar quantities of magnesium and chlorodiphenylphosphine in THF solution (total volume, 70 ml) gave 8.76 g (38.2%) of 2-*cis*-propenylphenyldiphenylphosphine (mp 72–77°) after purification by vacuum sublimation.

2-*trans*-Propenylphenyldiphenylphosphine (*trans*-PP).—Using the procedure described for the preparation of *o*-chloropropenylbenzene, 2-allylphenyldiphenylphosphine (16.6 g) was isomerized in an amyl alcohol solution of potassium hydroxide (10 g in 100 ml of alcohol). After removing the amyl alcohol by distillation under reduced pressure the residue was extracted with pentane. An attempt to crystallize the product from the filtered pentane extracts was not successful; therefore the pentane was removed under vacuum and the sample was purified by vacuum sublimation. A very viscous liquid (3.76 g, 23%) was obtained which vapor phase chromatography showed to contain less than 1% of the *cis* isomer. A product with the same physical properties and elemental analysis was obtained from *o*-chloro-*trans*-propenylbenzene by a Grignard reaction.

Complexes of Platinum(II).[10]—The ligand (0.60 g, 2.0 mmoles) in 20 ml of chloroform was added slowly (2 hr) to a stirred suspension of platinous bromide (1.20 g, 3.40 mmoles) in 40 ml of refluxing chloroform. After stirring for an additional 2 hr at reflux, the reaction mixture was filtered and the filtrate concentrated to *ca.* 5 ml. Addition of 80 ml of carbon tetrachloride followed by cooling to −78° gave a light brown solid which was washed with carbon tetrachloride. Recrystallization from 2:1 carbon tetrachloride–chloroform yielded yellow crystals of the platinum complex as a chloroform solvate. A chloroform-free product (*ca.* 0.8 g, 61%) was obtained by heating under vacuum at 110°.

Reaction of (AP)PtBr$_2$ with CN$^-$.—A suspension of the complex (0.1 g) in 30 ml of heptane and 10 ml of 10% aqueous potassium cyanide solution was heated to reflux, with stirring, for 12 hr. The two clear liquid phases which resulted were separated and the organic layer was washed thoroughly with water. Evaporation under vacuum followed by sublimation gave 0.03 g (65%) of 2-allylphenyldiphenylphosphine, identified by its infrared and nmr spectra.

Complexes of the Group VI Metals.—All of these complexes were prepared by displacement of norbornadiene from the appropriate norbornadiene group VI metal tetracarbonyl complex. The ligand (1 g, 3 mmoles) was heated under reflux with an equimolar amount of (norbornadiene)M(CO)$_4$ in 70 ml of benzene for 3 hr under an atmosphere of nitrogen. The benzene was then removed under vacuum and the residue extracted with 40 ml of pentane at −78°. The solid remaining was recrystallized from hexane to give air-stable, yellow crystals of the group VI metal complex in good yield (54–70%).

Reaction of the Presumed (AP)Mo(CO)$_4$ with Pyridine.—A solution of the complex (0.50 g) in 15 ml of freshly distilled pyridine was refluxed under nitrogen for 4 hr. The excess pyridine was removed at reduced pressure and the residue extracted with 40 ml of pentane. An orange solid, tentatively identified as a mixture of Mo(py)$_2$(CO)$_4$ and Mo(py)$_3$(CO)$_3$[11] on the basis of its infrared spectrum in the CO stretching region,[12] was collected

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(10) M. A. Bennett, H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 4570 (1964).

(11) E. W. Abel, M. A. Bennett, and G. Wilkinson, *ibid.*, 2323 (1959).

(12) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

cis-PP		(*cis*-PP)PtBr$_2$		(*cis*-PP)Cr(CO)$_4$		(*cis*-PP)Mo(CO)$_4$		(*cis*-PP)W(CO)$_4$	
Soln	Solid	Soln	Solid	Soln	Solid	Soln	Solid	Soln	Solid
	3067 sh		~3070 sh		3073 vw		3072 vw		3070 vw
	3053 w		3054 vw		3062 vw		3057 vw		3058 sh
			~3035 sh		3051 vw		3051 sh		3050 vw
	3012 vw		~3014 vw		3013 vw		3016 vw		3022 vw
	3005 sh				3001 vw		3001 vw		3001 vw
			2989 vw		2990 vw		2990 sh		2993 sh
	2965 vw		2950 vw		2954 vw		2959 vw		2956 vw
				2020 ms		2037 ms		2033 m	
				1931 s		1946 s		1938 s	
				1912 vs		1927 vs		1923 s	
								1912 s	
1642 vw		1445 sh?		1520 vw, b		1524 vw		1502 vw	
1582 w		1587 w		1582 w		1582 w		1582 w	
		1570 vw		1567 vw, b		1567 vw, b		~1567 vw, b	
1479 w		1484 w		1484 w		1481 w		1481 w	
1460 w		1473 w		1462 w		1460 w		1460 w	
1435 m		1439 m		1435 m		1435 m		1435 m	
		1416 vw							
1397 vw		1383 w		1391 w		1391 w		1389 w	
1364 w		1362 w		1364 w		1362 w		1362 w	
1325 vw		1330 vw		1326 vw		1326 vw		1328 vw	
1307 vw		1307 vw		1305 vw		1305 vw		1305 vw	
	1091 w, b		1099 m		1095 m		1096 m		1098 m
	1025 mw		1037 w		1034 mw		1032 mw		1035 mw
	927 w		903 w		907 w, b		910 w		906 mw, b
	814 mw		807 w		817 w		812 w		814 w
			784 w		788 w		771 w		787 w
	767 ms		764 m		761 m		760 m		762 m
	743 s		745 w		748 ms		747 ms		748 ms
			709 s						
					704 ms		701 ms		703 ms
	694 s		690 s		693 ms		693 ms		693 ms
					664 s		681 ms		

medium; mw, medium weak; w, weak; vw, very weak; b, broad; sh, shoulder. [c] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

by filtration. The filtrate was evaporated to dryness and the residue purified by sublimation. An oily solid (0.25 g, 84%) was obtained which was identified as 2-propenylphenyldiphenylphosphine[13] by its infrared and nmr spectra.

Results

2-Allylphenyldiphenylphosphine reacts with a suspension of platinous bromide in chloroform to give a monomeric complex of the formula $C_{21}H_{19}PPtBr_2$. Coordination through the carbon–carbon double bond is indicated by the absence of the band (1637 cm^{-1}) assigned to the C=C stretching frequency of the uncoordinated double bond in the infrared spectrum of the complex.

Our assignment of the new band at 1492 cm^{-1} in this infrared spectrum (Table II) to the coordinated C=C stretching frequency gives a frequency lowering upon coordination (145 cm^{-1}) of the same order as that observed for other platinum–olefin complexes.[14] Furthermore, the chelate complex reacts with CN$^-$, liberating the orginal ligand.

Similarly, air-stable, monomeric complexes of the general formula $C_{21}H_{19}PM(CO)_4$ result from the reaction between AP and the norbornadiene tetracarbonyl complexes of the group VI metals, whose infrared spectra are consistent with bidentate coordination of the olefinic ligand. However, the ligand which is displaced from these complexes is shown by nmr spectroscopy to be the isomeric product 2-propenyl phenyldiphenylphosphine.

The presence of the propenyl group in the coordinated ligand is also evidenced by the proton magnetic resonance spectra obtained for the complexes in deuteriochloroform solution (Figure 1). The relative areas (1:1:3) and chemical shift values relative to TMS (Table III) of the three groups of peaks upfield of the intense benzene–hydrogen absorption are entirely consistent with the $-CH{=}CHCH_3$ structure.[15] Moreover, the spin–spin coupling between the chemically different hydrogens in this structure, if the chemical shift values are sufficiently greater than the coupling constants, should give rise to a double quartet pattern for the olefinic hydrogen adjacent to the methyl group and a doublet for both the methyl group and the other olefinic hydrogen. With the addition of four-bond P^{31}–H coupling (J = 4.3 cps) to explain the further splitting of the doublet due to the olefinic hydrogen adjacent to the phenyl ring, this scheme quite adequately describes the detailed splitting pattern observed.

As an aid to establishing the geometric configuration of the propenyl olefin in these complexes, both the *cis* and *trans* isomers of 2-propenylphenyldiphenylphosphine were synthesized. These were prepared from the same basic starting material used in the preparation of AP, *o*-chloroallylbenzene. Isomerization in alcoholic

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[13] This was mostly the *cis* isomer although a significant amount (*ca.* 28%) of the *trans* isomer was also present, as evidenced by nmr spectroscopy.

[14] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[15] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 238.

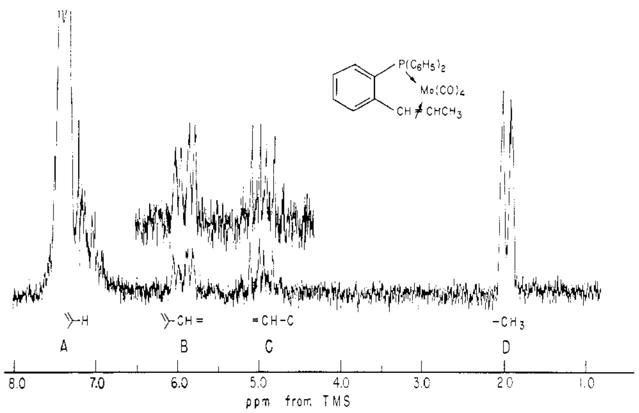
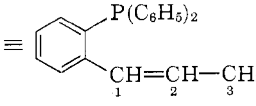


Figure 1.—Proton nmr spectrum of (*cis*-PP)Mo(CO)$_4$ in deuteriochloroform (saturated solution). Peak A arises from the benzene-ring protons; peaks B, C, and D, from the propenyl group.

Table III

Nmr Data for 2-Propenylphenyldiphenylphosphine and Its Complexes

PP ≡



Compound	Chemical shift values[a] δ_1	δ_2	δ_3	Spin–spin coupling constants, cps J_{12}	J_{23}
cis-PP	6.72	5.64	1.55	11.6	7.0
(*cis*-PP)Cr(CO)$_4$	5.56	4.58	1.84	10.0	6.2
(*cis*-PP)Mo(CO)$_4$	5.92	4.96	1.97	10.5	6.3
(*cis*-PP)W(CO)$_4$	5.58	4.67	2.18	10.0	6.2
trans-PP	. . .	6.00	1.69	15.6	6.7
(*trans*-PP)Mo(CO)$_4$	5.64	4.38	1.92	13.4	5.9

[a] In ppm from TMS; all values negative with respect to TMS.

KOH gave almost exclusively *o*-chloro-*trans*-propenylbenzene from which the *cis* isomer was obtained by ultraviolet irradiation. Conversion of the *o*-chloropropenylbenzenes to the diphenylphosphine derivatives, by means of a Grignard reaction, took place without isomerization.

The band at 959 cm^{-1} in the infrared spectra of the *trans*-propenyl compounds, assigned to the olefinic hydrogen out-of-plane deformation, as well as the band at 767 cm^{-1} in the spectra of the *cis*-propenyl compounds (Table II), served to distinguish the isomeric forms.[16] In addition, owing to the difference in the chemical shift values for the propenyl hydrogens and the larger coupling constant between the *trans* olefinic hydrogens (Table III),[17] nmr spectroscopy provided an independent method of identification.

The group VI metal complexes of these ligands were prepared by the same procedure used for the complexes of AP. Both ligands replaced norbornadiene in the coordination sphere of the group VI metal without isomerization to give compounds of the general formula, $C_{21}H_{19}PM(CO)_4$. As with the free ligands, the relative magnitudes of the *cis* and *trans* olefinic hydrogen coupling constants served to distinguish the isomeric compounds (Table III).

Comparison of the infrared and nmr spectra of these compounds with those of the original group VI metal complexes reveals that in each case the major product of the isomerization of the ligand, AP, is 2-*cis*-propenylphenyldiphenylphosphine.[17a]

Discussion

It has already been demonstrated that certain metal carbonyls are effective catalysts for the isomerization of olefins. The carbonyls and carbonyl hydrides of cobalt[18] and iron[19,20] and, in at least one instance, a group VI carbonyl[19] have been used to isomerize nonconjugated dienes to the conjugated species and various terminal monoolefins to a mixture of the internal isomers. The over-all isomer distribution in these cases tends to parallel the thermal equilibrium composition and when geometrical isomerization is possible the *trans*-olefins invariably predominate. In fact, allylbenzene, a close relative of the ligand AP, gives almost exclusively *trans*-propenylbenzene upon isomerization with Fe(CO)$_5$[21] or DCo(CO)$_4$.[22]

In view of the fact that *cis* olefins generally give more stable metal–olefin complexes than the corresponding *trans* isomers,[23] it would seem reasonable that complexation with the group VI metal has made the *cis* isomer of 2-propenylphenyldiphenylphosphine the thermodynamically favored product in the isomerization of AP. However, a preliminary investigation carried out on the molybdenum complexes has shown that the *cis*- and *trans*-PP complexes can be interconverted in refluxing heptane solution and that the equilibrium is decidedly in favor of the *trans* derivative.[24]

Therefore, the isolation of the *cis*-PP complex as the main product of the AP isomerization must be ascribed instead to its faster rate of formation under the reaction conditions employed.[25] A detailed examination of this unusual isomerization reaction is currently underway in our laboratories.

The lowering in the C=C stretching frequency ($\Delta\nu_{C=C}$), which occurs upon coordination of an olefin to a metal, is commonly taken as a measure of the

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(16) R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).

(17) See, for example, ref 15, p 241.

(17a) Note Added in Proof.—It has recently been found that a small amount of the isomeric *trans*-PP complex (*ca.* 10%) is also produced in these reactions, but due to a higher solubility in hydrocarbon solvents it is separated from the more predominant *cis*-PP complex in the purification procedure.

(18) I. Wender, S. Metlin, S. Ergun, H. W. Sternberg, and H. Greenfield, *J. Am. Chem. Soc.*, **78**, 5401 (1956); R. Heck and D. Breslow, *ibid.*, **83**, 4023 (1961).

(19) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

(20) J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2954 (1961); F. Asinger, S. Fell, and K. Schrage, *Chem. Ber.*, **98**, 372, 381 (1965); M. D. Carr, V. V. Kane, and M. C. Whiting, *Proc. Chem. Soc.*, 408 (1964).

(21) P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 6416 (1965).

(22) L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965).

(23) R. G. Guy and B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, **4**, 102 (1962).

(24) G. V. Nelson and L. V. Interrante, unpublished research.

(25) A similar situation has been observed in the isomerization of 1-butene by a rhodium catalyst [R. Cramer, *J. Am. Chem. Soc.*, **88**, 2272 (1966)]. In this case *cis*-2-butene is the predominant product in the early stages of the reaction owing to a faster rate of production from 1-butene although the more stable *trans* isomer eventually predominates.

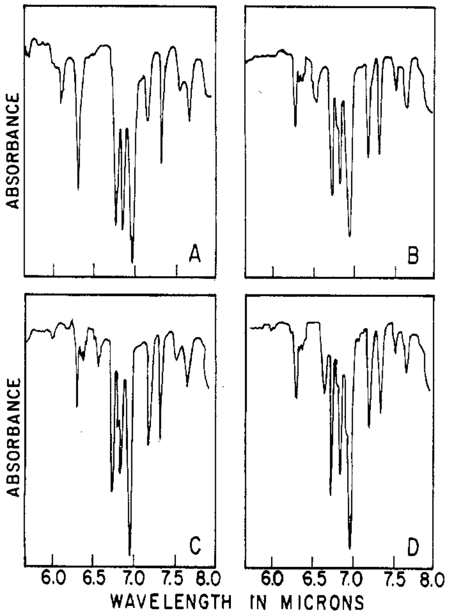

Figure 2.—Infrared spectra of 2-*cis*-propenylphenyldiphenylphosphine (*cis*-PP) and its group VI metal complexes in deuteriochloroform solution: A, *cis*-PP; B, (*cis*-PP)Mo(CO)$_4$; C, (*cis*-PP)Cr(CO)$_4$; D, (*cis*-PP)W(CO)$_4$.

metal–olefin bond strength.[14] Frequency lowerings as high as 187 cm^{-1} have been reported for Pt(II) complexes;[26] however, $\Delta\nu_{C=C}$ usually lies below 150 cm^{-1} and depends upon the nature of the olefin as well as the metal.[14,27]

In the case of the group VI metal complexes of *cis*-PP, determination of $\Delta\nu_{C=C}$ is simplified by the absence of bands in the region between 1480 and 1580 cm^{-1} in the infrared spectrum of the uncoordinated ligand (Figure 2). The new band that appears in this region in the spectra of the group VI metal complexes has been assigned to the coordinated C=C stretching vibration (Table II) giving a $\Delta\nu_{C=C}$ of 140, 122, and 118 cm^{-1} for W(0), Cr(0), and Mo(0), respectively. Therefore, metal–olefin bond strength appears to vary with the metal in this homologous series in the order W > Cr > Mo. This observation is in agreement with the order of M–C force constants determined for the group VI metal hexacarbonyls[28] and also fits in with the somewhat greater stability observed for the tungsten complexes of the simple monoolefins as compared with those of the other group VI metals.[29]

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Organometallic Compounds with Metal–Metal Bonds. IV. Pentacarbonylmanganese and Pentacarbonylrhenium Derivatives of Silicon, Germanium, Tin, and Lead. Preparation and Infrared and Nuclear Magnetic Resonance Studies[1]

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Carbonyl stretching frequencies and force constants calculated by the Cotton–Kraihanzel method are reported for the compounds $(C_6H_5)_3M\text{–}M'(CO)_5$ (M = Si, Ge, Sn, Pb; M' = Mn, Re) and for trimethyltin, trichlorotin, and tribromotin derivatives of manganese and rhenium. From a comparison of the force constants with those of related compounds, it is concluded that the trihalogenotin group is a strong π-acceptor ligand. The nmr spectra of the trimethyltin compounds and of $(CH_3)_2Sn[M'(CO)_5]_2$ are reported and the trend in proton–tin coupling constants is discussed in terms of enhanced s character in the tin–transition metal bond.

Introduction

Many compounds are now known in which the congeners of carbon in main group IV are covalently bonded to transition metals.[2] In descending this group, one passes from the extensively studied organometallic compounds to the newer field of metal–metal bonding. It appeared that the study of trends in this series would be of value.

The compounds $R_3M\text{–}M'(CO)_5$ (R = CH$_3$, C$_6$H$_5$, or halogen; M = Si, Ge, Sn, or Pb; M' = Mn or Re) form a particularly suitable series for such an investigation. The nature of the M–M' interaction can be

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[2] For leading references, *cf.* H. R. H. Patil and W. A. G. Graham, *ibid.*, **5**, 1401 (1966).