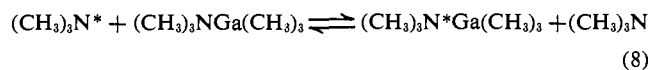


ergy values of 17.2 and 16.6 kcal/mole, respectively. Within experimental error this value agrees with the gas-phase dissociation energy of 17.6 kcal/mole for the adduct $(\text{CH}_3)_3\text{NB}(\text{CH}_3)_3$. At -24° the entropy of activation is $+15.0$ eu. This result contrasts with the findings of Oliver and coworkers on the corresponding $\text{Ga}(\text{CH}_3)_3^4$ and $\text{In}(\text{CH}_3)_3^5$ systems. Here no significant line broadening was apparent upon cooling, thus suggesting the availability of a low-energy reaction mechanism which is probably of the SN_2 type, *viz.*



The most obvious rationale for the difference in reaction mechanism between $(\text{CH}_3)_3\text{B}$ and the heavier group III alkyls would relate to the small size of boron and inavailability of d orbitals. However, this cannot be

the complete answer since the amine- BF_3 + excess amine reaction appears to go *via* an SN_2 process.^{3b} Thus, the reason might be simply one of lesser steric bulk around the boron atom in BF_3 than in $\text{B}(\text{CH}_3)_3$. Henold and Oliver⁵ have shown that reducing the steric bulk around nitrogen can shift the reaction to a lower energy (bimolecular) mechanism. Clearly more effort needs to be expended in order to elucidate the course of this type of exchange reaction. Toward this end, Shore and coworkers are studying the corresponding trimethylphosphine-trimethylborane system.

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The Lewis Basicity and Ligand Behavior of Cyclopropylphosphines

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Abstract: The preparation and properties of tricyclopropylphosphine and cyclopropyldiphenylphosphine are described. Tricyclopropylphosphine is a stronger Lewis base than $(i\text{-C}_3\text{H}_7)_3\text{P}$ toward the Lewis acids $\text{B}(\text{CH}_3)_3$, BF_3 , and BH_3 . Tricyclopropylphosphine will react with cyclopropyl bromide to yield $(c\text{-C}_3\text{H}_5)_3\text{P}^+\text{Br}^-$, which appears to be stable only in the solid state. The P-S and P-Se stretching frequencies of $(c\text{-C}_3\text{H}_5)_3\text{PS}$, $(c\text{-C}_3\text{H}_5)_3\text{PSe}$, and $(i\text{-C}_3\text{H}_7)_3\text{PS}$ are all higher than the values reported previously¹⁵ for tri(*n*-alkyl)- and tri(aryl)phosphine chalcogenides. The mono- and disubstituted tungsten carbonyl complexes of $(c\text{-C}_3\text{H}_5)_3\text{P}$ and $(c\text{-C}_3\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}$ have been prepared and the ^{31}P nmr chemical shifts of the free and complexed phosphines determined. The coordination chemical shifts of both phosphines are anomalously small. The ^{183}W - ^{31}P coupling constants and E species CO stretching frequencies of the (phosphine) $\text{W}(\text{CO})_5$ compounds fit the linear relationship of Grim, *et al.*, and suggest that the cyclopropylphosphines behave as π -acceptor ligands. Attempts to prepare an anion radical from $(c\text{-C}_3\text{H}_5)_3\text{P}$ or $(c\text{-C}_3\text{H}_5)_3\text{PO}$ were unsuccessful.

The cyclopropyl group can behave either as a π -electron donor or a π -electron acceptor. The former behavior is the best documented and is exemplified by a variety of structural studies which establish a preference for the "bisected" cyclopropyl conformation in π systems¹ and carbonium ions.² Acceptance of π electrons has been noted in certain cyclopropyl-substituted anion radicals.³ Here conjugation from an external p orbital to the intraannular orbitals of the cyclopropyl moiety apparently results in the "symmetrical" conformation.

In principle then the cyclopropyl group should resemble an aryl group in its ability to conjugate with systems with low-lying vacant d orbitals. For tertiary phosphines the conjugative interaction is considered to involve a balance between phosphorus lone pair \rightarrow ring

(p_π - p_π) donation and ring \rightarrow vacant phosphorus 3d orbital (p_π - d_π) acceptance.⁴ While the present study was in its infancy, Denny and Gross⁵ described the preparation of tricyclopropylphosphine and concluded that there is no conjugation between phosphorus and the cyclopropyl moiety on the basis of pK_a measurements. Recognizing that the presence of π bonding in the P-C linkage would be a very subtle effect which might not be manifest in the Brønsted basicity of a phosphine, we have directed our attention to assessing the Lewis basicity and ligand behavior of cyclopropyl-substituted phosphines.

Experimental Section

All volatile materials were handled in standard high-vacuum manifolds with U-traps interconnected with either Stock-type

(1) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647, (1965); J. P. Guillory and L. S. Bartell, *ibid.*, **43**, 654 (1965); L. S. Bartell, J. P. Guillory, and A. P. Parks, *J. Phys. Chem.*, **69**, 3043 (1965); G. L. Closs and B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965); G. R. DeMare and J. S. Martin, *ibid.*, **88**, 5033 (1966); G. A. Russell and H. Malkus, *ibid.*, **89**, 160 (1967).

(2) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965).

(3) N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967).

(4) J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *ibid.*, **90**, 5236 (1968), and references therein. For C_6F_5 -substituted phosphines, see M. G. Hogben, R. S. Gay, and W. A. G. Graham, *ibid.*, **88**, 3457 (1966).

(5) D. B. Denny and F. J. Gross, *J. Org. Chem.*, **32**, 2445 (1967). Prior to this work the synthesis of cyclopropyltriphenylphosphonium bromide had been reported; see D. T. Longone and R. R. Doyle, *Chem. Commun.*, 300 (1967), and references therein.

Table I. Volatility of Tricyclopropylphosphine^a

Temp, °C	25.40	33.75	40.80	46.90	50.90	53.70	59.00	68.00
P_{obsd} , mm	2.10	3.15	4.39	5.73	6.72	7.61	9.64	14.14
P_{calcd} , mm	2.01	3.06	4.31	5.71	6.84	7.73	9.70	14.04

^a Log $P_{\text{mm}} = 7.072 - 2021.2/T$, for temperatures from 25 to 75°.

mercury valves or stopcocks greased with Apiezon L. Materials of low volatility were handled in a helium-filled drybox. Vapor pressures were determined in an immersible tensimeter.

Materials. Diborane,⁶ $(\text{CH}_3)_3\text{B}$,⁷ and $(c\text{-C}_3\text{H}_5)_3\text{B}$ ⁸ were prepared by previously described procedures and purified until their vapor tensions and ir absorptions conformed to the literature values. Triphenyl phosphite, $(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)$, PCl_3 , BF_3 , $\text{W}(\text{CO})_6$, S, Se, Li, Mg, $c\text{-C}_3\text{H}_5\text{Br}$, and $i\text{-C}_3\text{H}_7\text{Br}$ were procured commercially and used without further purification. The solvents CH_2Cl_2 , THF (tetrahydrofuran), glyme (1,2-dimethoxyethane), and diglyme [bis(2-methoxyethyl) ether] were dried and distilled prior to use.

Tricyclopropylphosphine can be prepared in yields up to 80% by the reaction of cyclopropyllithium with triphenyl phosphite.⁶ However, contrary to a previous report,⁶ it may also be prepared (~10% yield) by the standard Grignard method using either THF or ether as a solvent. *Anal.*⁹ Calcd for $\text{C}_9\text{H}_{15}\text{P}$: C, 70.11; H, 9.81. Found: C, 69.95; H, 9.63. Principle ir bands (cm^{-1}) were at 3070, 2990, 1460, 1428, 1191, 1175, 1095, 1055, 1030, 1018, 913, 894, 874, 826, 795, 663, 610. The pmr spectrum consists of an extremely complex multiplet at τ 9.6.

Despite its low volatility (Table I) $(c\text{-C}_3\text{H}_5)_3\text{P}$ is reactive toward a variety of stopcock greases; hence all quantitative measurements were made in grease-free systems.

Triisopropylphosphine can be prepared in ~40% yields by the reaction of $i\text{-C}_3\text{H}_7\text{MgBr}$ with PCl_3 in ether solution followed by hydrolysis with saturated NH_4Cl solution and work-up in the usual manner. Triisopropylphosphine is a clear, colorless liquid, bp 48° (0.4 mm). *Anal.* Calcd for $\text{C}_9\text{H}_{21}\text{P}$: C, 67.47; H, 13.20. Found: C, 67.41; H, 13.27. Principal ir bands (cm^{-1}) were at 2950, 2870, 1460, 1386, 1370, 1215, 1195, 1150, 1097, 1040, 1019, 930, 887, 660, 580. The pmr spectrum exhibits a doublet of doublets (methyl protons) at τ 9.0 and a septet (α -hydrogen) at τ 8.3.

Cyclopropyldiphenylphosphine. A solution of 66.0 g (0.34 mole) of $(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)$ in 50 ml of ether was added dropwise with stirring to a solution of $c\text{-C}_3\text{H}_5\text{Li}$ ¹⁰ made from 48.4 g (0.4 mole) of $c\text{-C}_3\text{H}_5\text{Br}$ and 5.55 g (0.8 mole) of Li in 220 ml of ether. The flask was held at 0° throughout the addition. Following the addition the mixture was refluxed for 1.5 hr, then hydrolyzed at 0° with 100 ml of saturated NH_4Cl solution. The ether was removed *in vacuo* and the residue vacuum distilled (bp 100° (0.15 mm)) to yield ~37 g (48%) of $(c\text{-C}_3\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}$. *Anal.* Calcd for $\text{C}_{15}\text{H}_{15}\text{P}$: C, 79.63; H, 6.68. Found: C, 79.84; H, 6.66. The air-stable phosphine slowly crystallizes on standing (mp 47°). Principal ir bands (cm^{-1}) were at 3070, 2995, 1485, 1435, 1190, 1095, 1028, 895, 830, 745, 700, 660, 510, 485. The pmr spectrum of the neat phosphine consists of phenyl absorptions at τ 2.5 and 2.9 and a cyclopropyl absorption at τ 9.3.

Tricyclopropylphosphine sulfide was prepared in the drybox by direct reaction of the phosphine with a slight excess of sulfur. The reaction was exothermic and the yield was nearly quantitative. The hygroscopic, sublimable crystals melt at 53°. *Anal.* Calcd for $\text{C}_9\text{H}_{15}\text{PS}$: C, 58.04; H, 8.12. Found: C, 58.17; H, 8.07. The ir data relating to the P-S stretching region for this and subsequent phosphine sulfides and selenides are presented in Table III.

Triisopropylphosphine sulfide was prepared in an analogous manner. The colorless, air-stable crystals may be purified by sublimation, mp 35°. *Anal.* Calcd for $\text{C}_9\text{H}_{21}\text{PS}$: C, 56.21; H, 11.00. Found: C, 56.09; H, 10.33.

(6) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952).

(7) W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **28**, 777 (1958).

(8) A. H. Cowley and T. A. Furtch, *J. Am. Chem. Soc.*, **91**, 39 (1969).

(9) Analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mulheim (Ruhr), West Germany; Gailbraith Laboratories, Knoxville, Tenn.; or Chemalytics, Tempe, Ariz.

(10) D. Seyferth and H. M. Cohen, *J. Organometal. Chem.*, **1**, 15 (1963).

Tricyclopropylphosphine selenide, mp 44°, was prepared in an analogous manner by the direct reaction of the phosphine with elemental selenium. *Anal.* Calcd for $\text{C}_9\text{H}_{15}\text{PSe}$: C, 46.36; H, 6.48. Found: C, 46.18; H, 6.48.

Tricyclopropylphosphine oxide⁶ was prepared by aerial oxidation of $(c\text{-C}_3\text{H}_5)_3\text{P}$. These crystals are very hygroscopic and may be purified by sublimation *in vacuo*. *Anal.* Calcd for $\text{C}_9\text{H}_{15}\text{OP}$: C, 63.52; H, 8.88. Found: C, 63.32; H, 8.83.

Tetracyclopropylphosphonium bromide was prepared by combining equimolar amounts of $(c\text{-C}_3\text{H}_5)_3\text{P}$ and $c\text{-C}_3\text{H}_5\text{Br}$ in either ether or CH_2Cl_2 . In the case where ether is used as a solvent, some solid precipitated from solution. When all volatiles were pumped off, a white solid remained. *Anal.* Calcd for $\text{C}_{12}\text{H}_{20}\text{PBr}$: C, 52.38; H, 7.33. Found: C, 52.60; H, 7.33. The compound is air sensitive, apparently decomposing to $(c\text{-C}_3\text{H}_5)_3\text{PO}$ and $c\text{-C}_3\text{H}_5\text{Br}$. The pmr of solutions of the phosphonium salt consists of peaks attributable to free $(c\text{-C}_3\text{H}_5)_3\text{P}$ and $c\text{-C}_3\text{H}_5\text{Br}$, even down to -100°.

Triisopropylphosphinetungsten pentacarbonyl was prepared in diglyme solution using the published procedure.¹¹ The compound is a white solid, mp 150–160 dec, which decomposes slowly in air and *in vacuo*, and decomposes rapidly in CH_2Cl_2 solution. *Anal.* Calcd for $\text{C}_{14}\text{H}_{21}\text{O}_5\text{PW}$: C, 34.73; H, 4.37. Found: C, 34.81; H, 4.47. The disubstituted compound [$(i\text{-C}_3\text{H}_7)_2\text{P}$] $\text{W}(\text{CO})_4$ was not detected among the reaction products. In this and subsequent reactions monitoring of the mono-, *cis*-di-, and *trans*-disubstituted compounds was done by ir spectroscopy of cyclohexane solutions as described in detail by Grim and coworkers.^{11,12}

Tricyclopropylphosphinetungsten pentacarbonyl could not be prepared in useful yields by the standard procedure.¹¹ It was prepared in ~60% yield by irradiation of a solution of 5 g (14.2 mmoles) of $\text{W}(\text{CO})_6$ in ether solution with 0.55 g (3.6 mmoles) of $(c\text{-C}_3\text{H}_5)_3\text{P}$ using a medium-pressure mercury lamp (Hanovia, 450 W, Vycor filter) for 20 min.¹³ Purified $(c\text{-C}_3\text{H}_5)_3\text{PW}(\text{CO})_5$ is a white solid, mp 100–102°. *Anal.* Calcd for $\text{C}_{14}\text{H}_{15}\text{O}_5\text{PW}$: C, 35.17; H, 3.16. Found: C, 35.92; H, 4.06. The pmr spectrum consisted of a cyclopropyl resonance at τ 9.2.

Cyclopropyldiphenylphosphinetungsten pentacarbonyl, mp 127°, was made in ~10% yields by the diglyme reaction¹¹ and in ~40% yields by heating equimolar quantities of $(c\text{-C}_3\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}$ and $\text{W}(\text{CO})_6$ in a Pyrex tube for 3 hr at 155°. *Anal.* Calcd for $\text{C}_{20}\text{H}_{15}\text{O}_5\text{PW}$: C, 43.66; H, 2.75. Found: C, 44.36; H, 2.89.

trans-Bis(cyclopropyldiphenylphosphine)tungsten tetracarbonyl, mp 186°, was produced in both of the $(c\text{-C}_3\text{H}_5)(\text{C}_6\text{H}_5)_2\text{PW}(\text{CO})_5$ preparations. In the case of the diglyme reaction, it constituted the major product (~70%), and in the sealed tube reaction it represented ~20% of the total product. *Anal.* Calcd for $\text{C}_{34}\text{H}_{30}\text{O}_4\text{P}_2\text{W}$: C, 54.56; H, 4.04. Found: C, 53.43; H, 3.88. The *trans* stereochemistry of the disubstituted compound is assigned on the basis of the C–O stretching frequencies.^{11,12} The mono and bis compounds were easily separated by fractional crystallization.

trans-Bis(tricyclopropylphosphine)tungsten tetracarbonyl, mp 118°, was the major product in either the diglyme or the sealed-tube reaction of $(c\text{-C}_3\text{H}_5)_3\text{P}$ with $\text{W}(\text{CO})_6$ in the temperature range 155–160°, despite the fact that a wide variety of phosphine/ $\text{W}(\text{CO})_6$ ratios was used. *Anal.* Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_4\text{P}_2\text{W}$: C, 43.73; H, 5.01; mol wt, 612. Found: C, 43.99; H, 5.00; mol wt, 630. The pmr consisted of a cyclopropyl resonance at τ 9.2. Only trace amounts of the monosubstituted compound, $(c\text{-C}_3\text{H}_5)_3\text{PW}(\text{CO})_5$, could be isolated by column chromatography of the crude reaction product.

Lewis Basicity Experiments. In all of the Lewis basicity experiments, equimolar quantities (usually 0.5 mmole) of tricyclopropylphosphine and/or triisopropylphosphine were transferred into an nmr tube in a helium-filled drybox. The tube was then quickly attached to a vacuum line and 1.0 ml of CH_2Cl_2 was distilled into

(11) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Am. Chem. Soc.*, **89**, 5573 (1967).

(12) S. O. Grim and D. A. Wheatland, private communication.

(13) W. Strohmeier and D. von Hobe, *Z. Physik. Chem. (Frankfurt)*, **34**, 393 (1962).

Table II. Nmr Data for Borane Complexes

Complex	Temp, °C	τ^a	$\delta(^{11}\text{B})^b$	$\delta(^{19}\text{F})^c$	Coupling constants, Hz
$(c\text{-C}_3\text{H}_5)_3\text{PB}(\text{CH}_3)_3$	Ambient	10.12	$J_{\text{PBCH}} = 0$
	-80	10.39	$J_{\text{PBCH}} = 16.7$
$(i\text{-C}_3\text{H}_7)_3\text{PB}(\text{CH}_3)_3$	Ambient	9.94	$J_{\text{PBCH}} = 0$
	-80	10.31	$J_{\text{PBCH}} = 13.8$
$(c\text{-C}_3\text{H}_5)_3\text{PBH}_3$	Ambient	...	+66.8	...	$J_{\text{BH}} = 94$; $J_{\text{PB}} = 74$
$(i\text{-C}_3\text{H}_7)_3\text{PBH}_3$	Ambient	...	+62.7	...	$J_{\text{BH}} = 95$; $J_{\text{PB}} = 60$
$(c\text{-C}_3\text{H}_5)_3\text{PBF}_3$	15	+158.9	$J_{\text{BF}} = 52.0$
	Ambient	+123.9	$J_{\text{PBF}} = 210.0$
$(i\text{-C}_3\text{H}_7)_3\text{PBF}_3$	Ambient	+123.9	$J_{\text{BF}} = 54.8$
					$J_{\text{PBF}} = 195.0$

^a ¹H chemical shifts of CH₃(B) protons in τ units (relative to internal CH₂Cl₂). ^b In ppm relative to external B(OCH₃)₃. ^c In ppm relative to external CCl₃F.

the tube^{14,15} with subsequent addition of an equimolar amount of the Lewis acid. In the pmr experiments CH₂Cl₂ was used as the internal standard; in the ¹¹B, ¹⁹F, and ³¹P experiments, B(OCH₃)₃, CCl₃F, and 85% H₃PO₄, respectively, were sealed in capillaries and used as external standards. Measurement of the relative concentrations of the adducts in the case of the $(c\text{-C}_3\text{H}_5)_3\text{P} + \text{B}(\text{CH}_3)_3$ system was achieved by curve analysis. The curves were traced with a magnetic pencil follower, digitized, and resolved into separate peaks with the aid of a program written for the CDC 6600 computer by Peter F. Rusch. The peaks were resolved to fit Lorentzian functions with the relative peak areas being part of the program output.

Attempts to produce anion radicals by sodium or sodium-potassium alloy reduction of $(c\text{-C}_3\text{H}_5)_3\text{P}$ or $(c\text{-C}_3\text{H}_5)_3\text{PO}$ in either glyme or THF were unsuccessful. Neither compound appeared to react with the alkali metals.

Infrared Spectra. Most of the infrared spectra were measured on a Perkin-Elmer Model 337 grating spectrometer. Some spectra were recorded on a Beckman IR 7 spectrophotometer equipped with NaCl and CsI optics. Vapor samples were run in a 100-mm gas cell fitted with KBr windows. Less volatile liquids were run as neat liquid films. Solids were run as KBr disks or in cyclohexane solution.

Nmr Spectra. Ambient-temperature ¹H nmr spectra were recorded on a Varian A-60 instrument. ¹¹B, ¹⁹F, ³¹P, and low-temperature ¹H spectra were recorded on a Varian HA-100 spectrometer.

Esr spectra were run on a Varian V-4502 X-band spectrometer.

Results

The chemical shift and coupling constant data for various borane complexes of $(c\text{-C}_3\text{H}_5)_3\text{P}$ and $(i\text{-C}_3\text{H}_7)_3\text{P}$ are presented in Table II. Competition reactions were performed by allowing 1:1:1 mixtures of $(c\text{-C}_3\text{H}_5)_3\text{P}$, $(i\text{-C}_3\text{H}_7)_3\text{P}$, and BX₃ (X = CH₃, H, or F) to equilibrate in CH₂Cl₂ solution. Accurate estimation of the equilibrium concentrations of the complexes was made difficult by the overlapping of peaks and intermolecular exchange. However, in the case of the $(c\text{-C}_3\text{H}_5)_3\text{P} + (i\text{-C}_3\text{H}_7)_3\text{P} + \text{B}(\text{CH}_3)_3$ competition reaction it was possible to resolve the overlapping doublets of the CH₃(B) resonances with the aid of a curve analysis procedure (see Experimental Section). On the basis of peak areas the relative concentrations of $(c\text{-C}_3\text{H}_5)_3\text{PB}(\text{CH}_3)_3$ and $(i\text{-C}_3\text{H}_7)_3\text{PB}(\text{CH}_3)_3$ were 2.7:1. The P-S and P-Se stretching frequencies for $(c\text{-C}_3\text{H}_5)_3\text{PS}$, $(i\text{-C}_3\text{H}_7)_3\text{PS}$, and $(c\text{-C}_3\text{H}_5)_3\text{PSe}$ are presented in Table III along with some of Zingaro's data¹⁶ on other phosphine chalcogenides. In the case of $(i\text{-C}_3\text{H}_7)_3\text{PS}$, the P-S stretching frequency is easily recognized as an intense band which is present in the sulfide but absent in the parent phosphine. The

(14) There was no apparent reaction between CH₂Cl₂ and either $(i\text{-C}_3\text{H}_7)_3\text{P}$ or $(c\text{-C}_3\text{H}_5)_3\text{P}$ even after several months; cf. $(\text{CH}_3)_3\text{P}$ and $(\text{CH}_3)_3\text{N}$ reaction with CH₂Cl₂.

(15) A. H. Cowley and J. L. Mills, *J. Am. Chem. Soc.*, **91**, 2911 (1969).

(16) R. A. Zingaro, *Inorg. Chem.*, **2**, 192 (1963).

Table III. P-S and P-Se Stretching Frequencies of Tertiary Phosphine Sulfides and Selenides

Compound	$\nu_{\text{P-S}}$	$\nu_{\text{P-Se}}$	Ref
$(\text{CH}_3)_3\text{P(X)}^a$	570	441	<i>b</i>
$(n\text{-C}_3\text{H}_7)_3\text{P(X)}$	596	496	<i>b</i>
	583		
$(i\text{-C}_3\text{H}_7)_3\text{P(X)}$	701	...	<i>c</i>
$(c\text{-C}_3\text{H}_5)_3\text{P(X)}$	727	685	<i>c</i>
$(c\text{-C}_6\text{H}_{11})_3\text{P(X)}$	619	543	<i>b</i>
$(\text{C}_6\text{H}_5)_3\text{P(X)}$	627	560	<i>b</i>
Cl ₃ P(S)	745	...	<i>d</i>
(NH ₂) ₃ P(S)	860	...	<i>e</i>

^a X = S or Se. ^b Reference 15. ^c This work. ^d F. N. Hooge and P. J. Christen, *Rec. Trav. Chim.*, **77**, 911 (1958). ^e E. Steger, *Z. Elektrochem.*, **61**, 1004 (1957).

assignment of the P-S and P-Se stretches of the cyclopropyl compounds is dealt with in the discussion.

The ³¹P chemical shift and coupling constant data for the free phosphines and the tungsten carbonyl complexes are presented in Table IV. The coordination chemical shift has been defined previously¹⁷ as $\delta_{\text{complex}} - \delta_{\text{free ligand}}$. The C-O stretching frequencies of the tungsten carbonyl complexes are listed in Table IV.

Discussion

In each of the three competition reactions, $(c\text{-C}_3\text{H}_5)_3\text{P}$ was found to be a stronger Lewis base than $(i\text{-C}_3\text{H}_7)_3\text{P}$ on the basis of the nmr peak areas. Only in the case of the $\text{B}(\text{CH}_3)_3$ reaction was it possible to obtain a quantitative measurement of the relative concentrations of the adducts at equilibrium. However, qualitatively the same conclusion can be drawn from the BH₃ and BF₃ reactions. Although these competition reactions could be taken to indicate that $(c\text{-C}_3\text{H}_5)_3\text{P}$ is a stronger donor than $(i\text{-C}_3\text{H}_7)_3\text{P}$, it is obvious that these results might be simply a reflection of the larger steric bulk of the isopropyl moiety.

At ambient temperature both the $\text{B}(\text{CH}_3)_3$ and BF_3 systems are undergoing rapid intermolecular exchange since, e.g., a 1:1:1 mixture of $(c\text{-C}_3\text{H}_5)_3\text{P}$, $(i\text{-C}_3\text{H}_7)_3\text{P}$, and $\text{B}(\text{CH}_3)_3$ exhibited only a singlet in the B-methyl region. Cooling the system to -80° resulted in the appearance of the anticipated pair of (overlapping) doublets. Several analogous cases of intermolecular exchange reactions involving Lewis acids and bases are now known.¹⁵ At first sight it appears that $(c\text{-C}_3\text{H}_5)_3\text{P}$ is a stronger Lewis base than $(\text{C}_6\text{H}_5)_3\text{P}$ since the latter produced only a trace (~1%) of the phosphonium salt

(17) S. O. Grim, R. L. Keiter, and W. McFarlane, *ibid.*, **6**, 1133 (1967).

Table IV. Structural Data for Phosphorus-Sulfur Compounds

Compound	P-S bond length, Å	P-C bond length, Å	Bond angles, deg
$(c\text{-C}_3\text{H}_5)_3\text{PS}^a$	1.939 ± 0.002	1.785	$\angle\text{SPC} = 113.4$ $\angle\text{CPC} = 105.2$
$(\text{C}_2\text{H}_5)_3\text{PS}^b$	1.864	1.865	$\angle\text{SPC} = 112$ $\angle\text{CPC} = 107$
$(\text{C}_2\text{H}_5)_4\text{P}_2\text{S}_2^c$	1.94 ± 0.01	1.83 ± 0.015	
$(\text{C}_6\text{H}_5)_2(\text{CH}_3)_2\text{P}_2\text{S}_2^d$	1.98	1.82 (CH ₃) 1.88 (C ₆ H ₅)	
Br_3PS^e	1.89 ± 0.06		$\angle\text{BrPBr} = 106$
Cl_3PS^f	1.85 ± 0.02		$\angle\text{ClPCl} = 100.5$
$\text{F}_3\text{PS}^f, g$	1.87 ± 0.03 1.86		$\angle\text{FPF} = 100.3$

^a Reference 20. ^b M. Van Meersche and A. L. Leonard, *Acta Cryst.*, **12**, 1053 (1959). ^c S. N. Dutta and M. M. Woolfson, *ibid.*, **14**, 178 (1961). ^d P. J. Wheatley, *J. Chem. Soc.*, 523 (1960). ^e J. H. Sechrist and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 1941 (1944). ^f Q. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952). ^g N. J. Hawkins, V. W. Cohen, and W. S. Koski, *ibid.*, **20**, 528 (1952).

Table V. ³¹P Chemical Shift and Coupling Constant Data for Phosphines and Tungsten Carbonyl Complexes

Compound	$\delta_{\text{free ligand}}^a$	$\delta_{\text{complex}}^a$	Coordination chemical shift	$J_{\text{ISW-}^{31}\text{P}}$, Hz
$(c\text{-C}_3\text{H}_5)_3\text{PW}(\text{CO})_5$	-17.1	-18.8	-1.7	242
$(i\text{-C}_3\text{H}_7)_3\text{PW}(\text{CO})_5$	-19.4 ^b	-41.0	-21.6	... ^c
$(\text{C}_6\text{H}_5)_2(c\text{-C}_3\text{H}_5)\text{PW}(\text{CO})_5$	-1.9	-19.4	-17.5	245
$(\text{C}_6\text{H}_5)_2(i\text{-C}_3\text{H}_7)\text{PW}(\text{CO})_5^d$	-0.2	-26.3	-26.1	240
$(\text{C}_6\text{H}_5)_3\text{PW}(\text{CO})_5^d$	6.0	-20.6	-26.6	280
$(n\text{-C}_4\text{H}_9)_3\text{PW}(\text{CO})_5^d$	32.3	6.4	-25.9	200
$\text{trans}[(c\text{-C}_3\text{H}_5)_3\text{P}]_2\text{W}(\text{CO})_4$	-17.1	-21.2	-4.1	280
$\text{trans}[(\text{C}_6\text{H}_5)_2(c\text{-C}_3\text{H}_5)\text{P}]_2\text{W}(\text{CO})_4$	-1.9	-25.2	-23.3	...

^a ³¹P chemical shifts relative to external 85% H₃PO₄. ^b ³¹P chemical shift for $(i\text{-C}_3\text{H}_7)_3\text{P}$ taken from S. O. Grim and W. McFarlane, *Nature*, **208**, 995 (1965). ^c Value impossible to obtain due to rapid decomposition of the complex. ^d All nmr data taken from ref 11.

upon standing with $c\text{-C}_3\text{H}_5\text{Br}$ for 1 week in a sealed tube.¹⁵ However, the facile reaction of $(c\text{-C}_3\text{H}_5)_3\text{P}$ with $c\text{-C}_3\text{H}_5\text{Br}$ to produce tetracyclopropylphosphonium bromide may relate to lattice energy considerations [$(c\text{-C}_3\text{H}_5)_3\text{P}$ is a liquid at ambient temperature]. In fact, the phosphonium salt $(c\text{-C}_3\text{H}_5)_4\text{PBr}$ dissociates completely in solution since only peaks attributable to $(c\text{-C}_3\text{H}_5)_3\text{P}$ and $c\text{-C}_3\text{H}_5\text{Br}$ are detectable in the pmr spectrum down to -100° .

It is evident (Table III) that the P-S stretching frequencies of both $(i\text{-C}_3\text{H}_7)_3\text{PS}$ and $(c\text{-C}_3\text{H}_5)_3\text{PS}$ are considerably higher than those of the tri(*n*-alkyl)- and tri(aryl)phosphine sulfides. The assignment of the P-S stretching mode in $(i\text{-C}_3\text{H}_7)_3\text{PS}$ seems unequivocal because only one band appears upon sulfurization of the phosphine. In the sulfurization of $(c\text{-C}_3\text{H}_5)_3\text{P}$ new bands appeared at 727 and 540 cm^{-1} . However, the 727- cm^{-1} band is more intense, and treatment of $(c\text{-C}_3\text{H}_5)_3\text{PS}$ with ICl shifted the band to 650 cm^{-1} which is comparable with the shifts noted by Zingaro¹⁶ for the ICl adducts of other phosphine sulfides. Essentially the same reasoning applies to the assignment of the P-Se stretching frequency of $(c\text{-C}_3\text{H}_5)_3\text{PSe}$. Presumably the high value for the P-S stretching frequency in $(i\text{-C}_3\text{H}_7)_3\text{PS}$ is due to the steric bulk of the isopropyl groups with consequent opening of the CPC bond angles. The only α -branched alkyl species in Zingaro's study¹⁶ is $(c\text{-C}_6\text{H}_{11})_3\text{PS}$. It is of interest to note that the P-S stretching frequency of this phosphine sulfide is 23 cm^{-1} higher than that of, e.g., $(n\text{-C}_4\text{H}_9)_3\text{PS}$. From the electronic standpoint the only trend which is evident from Table III is that an increase in the electro-negativity of the phosphorus substituents augments the

P-S stretching frequency, presumably because this facilitates $p_\pi\text{-d}_\pi$ back-bonding from sulfur to phosphorus. This argument gains support from the shorter P-S bond lengths of the thiophosphoryl halides (Table IV) compared with other compounds with P-S bonds. A similar argument obtains in the phosphine oxides, since Wagner's calculations¹⁹ indicate that the P-O bond order varies from one in $(\text{CH}_3)_3\text{PO}$ to almost three in F_3PO . Thus one possible implication of our data is that the cyclopropyl groups are withdrawing electrons from phosphorus. However, at this point it is not clear why this effect should be any more pronounced than with phenyl substituents. Furthermore, a recent X-ray crystallographic study²⁰ of $(c\text{-C}_3\text{H}_5)_3\text{PS}$ (Table IV) indicates that the P-S bond length is not shortened. It is interesting, however, that the PC bond length is somewhat shorter than usual.

Two lines of evidence suggest that $(c\text{-C}_3\text{H}_5)_3\text{P}$ behaves as a π -acceptor ligand in its tungsten carbonyl complexes. First, the most striking feature of the ³¹P chemical shift data (Table V) is the very small coordination chemical shift (*i.e.*, $\delta_{\text{complex}} - \delta_{\text{ligand}}$) of $(c\text{-C}_3\text{H}_5)_3\text{P}$ in both the mono- and disubstituted compounds. The value of 1.7 ppm for $(c\text{-C}_3\text{H}_5)_3\text{PW}(\text{CO})_5$ contrasts with the range 25-27 ppm noted by Grim, *et al.*,¹¹ for a variety of alkyl- and arylphosphine complexes of this type. The effect of the cyclopropyl moiety is also shown in the small coordination chemical shift (4.1 ppm) for $(c\text{-C}_3\text{H}_5)(\text{C}_6\text{H}_5)_2\text{PW}(\text{CO})_5$. The coordination chemical shift for $(i\text{-C}_3\text{H}_7)_3\text{PW}(\text{CO})_5$ is also on the small side, but this is not surprising in view of previous work with other phosphines bearing bulky groups.¹¹ The reasons which have been advanced for small coordination chemical

(18) E. E. Schweizer and J. G. Thompson, *Chem. Commun.*, 666 (1966).

(19) E. L. Wagner, *J. Am. Chem. Soc.*, **85**, 161 (1963).

(20) S. H. Simonsen and B. Bowen, submitted for publication.

Table VI. CO Stretching Frequencies (cm^{-1}) for Tungsten Carbonyl Complexes

Complex	A_1	B_1	A_1	E
$(c\text{-C}_3\text{H}_5)_3\text{PW}(\text{CO})_5$	2073 m ^a	1975 w	...	1936 vs
$(i\text{-C}_3\text{H}_7)_3\text{PW}(\text{CO})_5$	2068 m	1973 w	1942 sh	1932 vs
$(\text{C}_6\text{H}_5)_2(c\text{-C}_3\text{H}_5)\text{PW}(\text{CO})_5$	2075 m	1979 w	1946 sh	1939 vs
$\text{trans}-[(c\text{-C}_3\text{H}_5)_3\text{P}]_2\text{W}(\text{CO})_4$		1883 vs		
$\text{trans}-[(\text{C}_6\text{H}_5)_2(c\text{-C}_3\text{H}_5)\text{P}]_2\text{W}(\text{CO})_4$		1887 vs		

^a Legend: w = weak; m = medium; s = strong; and sh = shoulder.

shifts are (a) there is only a small hybridizational change as the phosphine coordinates, and (b) the phosphine is a good π acceptor. Reason a would be expected to apply to phosphines with bulky groups since the CPC bond angles are presumably quite wide and hence only small geometric changes ensue upon coordination. Since the steric bulk of the cyclopropyl group is less than that of the isopropyl group, reason a would not explain the coordination chemical shift of $(c\text{-C}_3\text{H}_5)_3\text{PW}(\text{CO})_5$ being any smaller than that of $(i\text{-C}_3\text{H}_7)_3\text{PW}(\text{CO})_5$ (21.6 ppm). Therefore, this type of argument suggests that $(c\text{-C}_3\text{H}_5)_3\text{P}$ is a good π acceptor. It is also of interest to note that we were unable to prepare $(c\text{-C}_3\text{H}_5)_3\text{PW}(\text{CO})_5$ by the usual reaction. Heating a mixture of $(c\text{-C}_3\text{H}_5)_3\text{P}$ with $\text{W}(\text{CO})_6$ in diglyme at 155–160° (the same temperature employed in the synthesis of a variety of (phosphine) $\text{W}(\text{CO})_5$ complexes¹¹) resulted in the almost exclusive formation of $\text{trans}-[(c\text{-C}_3\text{H}_5)_3\text{P}]_2\text{W}(\text{CO})_4$. This observation suggests that $(c\text{-C}_3\text{H}_5)_3\text{P}$ exerts a *trans*-labilizing effect.

The second argument for the π -acceptor character of $(c\text{-C}_3\text{H}_5)_3\text{P}$ concerns the relationship between the tungsten–phosphorus coupling constant, $J_{183\text{W}-31\text{P}}$, and the E species C–O stretch in $\text{R}_3\text{PW}(\text{CO})_5$ compounds. It is found that phosphines with electron-attracting groups have $J_{183\text{W}-31\text{P}}$ and ν_{CO} values and *vice versa*. Grim and coworkers¹¹ have interpreted these variations in terms of the π -acceptor ability of phosphines; *i.e.*, for phosphines bearing electron-attracting groups the metal–phosphorus σ bond is strengthened by a synergic π -bonding interaction; hence $J_{183\text{W}-31\text{P}}$ increases because of the increased per cent s character in the σ bond and/or *via* a π -coupling mechanism.²¹ As shown in Figure 1, both $(c\text{-C}_3\text{H}_5)_3\text{P}$ and $(c\text{-C}_3\text{H}_5)(\text{C}_6\text{H}_5)_2\text{P}$ fit on Grim's plot of $J_{183\text{W}-31\text{P}}$ *vs.* the E species C–O stretching frequency. Tricyclopropylphosphine adopts a position which is intermediate between the tri(*n*-alkyl)phosphines and $(\text{C}_6\text{H}_5)_3\text{P}$, thus suggesting that $(c\text{-C}_3\text{H}_5)_3\text{P}$ behaves as a mild π -acceptor ligand. Similarly, in the

(21) The metal–ligand π -bonding interpretation has been criticized by R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1761 (1967), on the basis of the C–O stretching frequencies in (amine) $\text{W}(\text{CO})_5$ complexes. However, for a reinterpretation of this interpretation, see R. P. Stewart and P. M. Treichel, *ibid.*, **7**, 1942 (1968), and references therein.

mixed phosphines, $(\text{C}_6\text{H}_5)_2\text{RP}$, the cyclopropyl derivative has a higher $J_{183\text{W}-31\text{P}}$ and ν_{CO} than its isopropyl counterpart. In the case of $(i\text{-C}_3\text{H}_7)_3\text{PW}(\text{CO})_5$, the ν_{CO} is lower than those of tri(*n*-alkyl)phosphine complexes. Unfortunately, we were unable to observe the tungsten–phosphorus coupling constant in this system due to the rapid deposition of paramagnetic impurities in the nmr sample. If the linear relationship between ν_{CO} and $J_{183\text{W}-31\text{P}}$ holds for $(i\text{-C}_3\text{H}_7)_3\text{PW}(\text{CO})_5$, we estimate the latter to be 184 Hz.

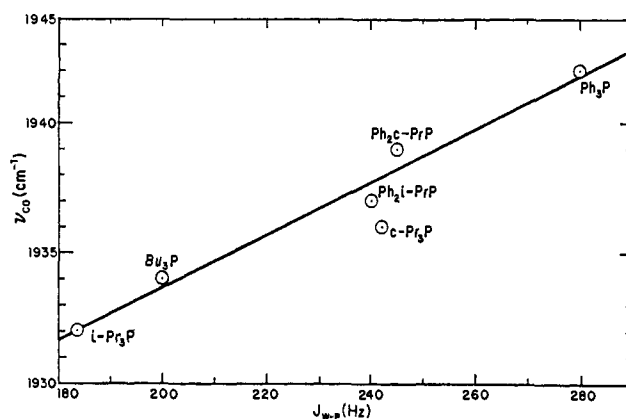


Figure 1. A plot of $^{183}\text{W}-^{31}\text{P}$ coupling constant *vs.* E species CO stretching frequency for some (phosphine) $\text{W}(\text{CO})_5$ complexes. See Tables V and VI for the pertinent literature references. The compound $(i\text{-C}_3\text{H}_7)_3\text{PW}(\text{CO})_5$ is assumed to lie on the straight line.

We were encouraged to attempt the preparation of anion radicals from $(c\text{-C}_3\text{H}_5)_3\text{P}$ and $(c\text{-C}_3\text{H}_5)_3\text{PO}$ to see if they behaved like the corresponding phenyl compounds,²² and to try to shed some light on the nature of the cyclopropyl–phosphorus linkage. However, neither sodium nor sodium–potassium alloy appeared to react with $(c\text{-C}_3\text{H}_5)_3\text{P}$ or $(c\text{-C}_3\text{H}_5)_3\text{PO}$ in the usual solvents.

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(22) A. H. Cowley and M. H. Hnoosh, *J. Am. Chem. Soc.*, **88**, 2595 (1966).