TABLE I
¹H NMR DATA OF COMPOUNDS OF THE TYPE [Ag(Xacac)(olefin)][d]

Compound	$\delta^c(-CH)$	$\delta(>CH_2)$	$\delta(>CH)^a$	$\delta(CH_3)$
[Ag(hfacac)(cyclooctadiene)]	3.70 (3.6)[b]	7.38 (8.3)	3.93 (1.1)	
[Ag(hfacac)(cyclooctatetraene)]	3.58 (8.0)		3.90 (1.0)	
[Ag(hfacac)(cyclooctene)]	3.90 (1.9)	7.55 (3.9)	4.09 (1.0)	
		8.41 (8.3)		
[Ag(hfacac)(cycloheptene)]	3.55 (2.0)	7.65 (3.8)	4.00 (1.3)	
		8.30 (5.9)		
[Ag(hfacac)(cyclohexene)]	3.64 (1.8)	7.71 (4.3)	4.02 (0.9)	
		8.27 (4.0)		
[Ag(tfacac)(cyclooctadiene)]	3.93 (3.8)	7.48 (7.9)	4.46 (1.2)	7.92 (3.1)
[Ag(tfacac)(cyclooctatetraene)]	3.83 (8.5)		4.43 (0.8)	7.91 (2.7)

a Methine proton on β-diketonate. *b* Integrated intensities in parentheses. *c* Chemical shifts reported using the τ scale with TMS as a standard. *d* X is hf or tf.

TABLE II
VIBRATIONAL FREQUENCIES OF SOME METAL β-DIKETONATES IN THE REGION 1600–1800 CM^{-1}

Compound	Frequencies
Pd(hfacac)$_2$[a]	1603
Rh(hfacac)(C$_8$H$_{14}$)$_2$[b]	1621, 1602
Cu(hfacac)$_2$[c]	1646, 1617
Pd(hfacac)$_2$(P(C$_6$H$_5$)$_3$)[d]	1768, 1723, 1656, 1629
Ag(hfacac)(P(C$_6$H$_5$)$_3$)$_2$[e]	1663, 1640 sh
Ag(hfacac)(C$_8$H$_{12}$)	1667, 1634
Ag(hfacac)(C$_8$H$_8$)	1660, 1636
Ag(hfacac)(C$_8$H$_{14}$)	1667, 1640 sh
Ag(hfacac)(C$_7$H$_{12}$)	1663, 1644 sh
Ag(hfacac)(C$_6$H$_{10}$)	1678, 1644, 1615
Ag(tfacac)(C$_8$H$_{12}$)	1635, 1620 sh
Ag(tfacac)(C$_8$H$_8$)	1645, 1625 sh

a Prepared by addition of sodium hexafluoroacetylacetonate to a palladium chloride suspension in hot water. Product sublimed at 90° (1 Torr). *b* Prepared by addition of potassium carbonate and hexafluoroacetylacetone to [RhCl(C$_8$H$_{14}$)$_2$]$_2$ in dichloromethane. Recrystallized from dichloromethane–petroleum ether. *c* Prepared by method given by C. H. Ke and N. C. Li, *J. Inorg. Nucl. Chem.*, **28**, 2255 (1966). *d* Prepared in a manner identical with that for Pd(acac)$_2$(P(C$_6$H$_5$)$_3$) given by S. Baba, T. Ogura, and S. Kawaguchi, *Inorg. Nucl. Chem. Lett.*, **7**, 1195 (1971). *e* D. Gibson, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 367 (1970).

Pd(hfacac)$_2$(P(C$_6$H$_5$)$_3$) is also consistent with this formulation. One observes the ν(C=O) modes in the carbon-bonded hfacac at 1768 and 1723 cm^{-1}. These absorptions are absent in the silver compounds indicative that the bonding of the hfacac to the silver is *via* the oxygen atoms.

The nmr spectra in chloroform-*d* are consistent with the formulation Ag(Xacac)(olefin). The chemical shifts of the coordinated olefinic protons are all approximately 0.6 ppm downfield (to a lower τ value) from the uncoordinated "free" olefin. Addition of free olefin to a solution of the silver olefin compounds results in an upfield shift of the olefinic peak indicative that a rapid dissociation of the olefin from the Ag(Xacac) moiety occurs in solution. This is commonly observed with silver olefin compounds.[5] This labile dissociation of the olefin moiety would explain why the chemical shift of all the olefinic protons in cyclooctatetraene are the same. The lability of the olefin–metal bond prevents definitive structural assignments *via* nmr from being made, such as the differentiation of oxygen and carbon bonding of the β-diketonate group. The nmr spectrum of Ag(C$_8$H$_8$)(hfacac) does not change significantly when cooled to −30°.

Molecular weight measurements indicate that Ag(hfacac)(cyclooctadiene) and Ag(hfacac)(cyclooctene)

are monomers in bromoform and Ag(hfacac)(cyclooctadiene) is partially polymeric in cyclohexane. The molecular weights of Ag(hfacac)(cyclooctadiene) and Ag(hfacac)(cyclooctatetraene) in benzene are lower than theoretically calculated for these compounds and correspond closely to the compound [Ag(hfacac)(benzene)] (mol wt 393). The conductance data suggest that [Ag(hfacac)(C$_8$H$_{12}$)] is nonionic in nitromethane.

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Titanium(III) Chloride–Bis(alkylphosphine) Complexes

BY C. D. SCHMULBACH,* C. H. KOLICH, AND C. C. HINCKLEY

Titanium(III) chloride–bis(alkylphosphine) complexes have been prepared by direct combination of the components in toluene at elevated temperature. The alkylphosphines include methylphosphine, dimethylphosphine, trimethylphosphine, and triethylphosphine. Attempts to prepare titanium trichloride complexes of the more weakly basic phosphorus trifluoride, phosphorus trichloride, and triphenylphosphine under a variety of experimental conditions were unsuccessful. The only other reported titanium(III) phosphine complex is TiCl$_3$·[(C$_2$H$_5$)$_2$P]$_2$C$_2$H$_4$.[1]

These complexes are soluble in benzene and the molecular weight of the triethylphosphine adduct in benzene was shown by freezing point depression to be equal to that of the titanium(III) chloride–bis(triethylphosphine) monomer. The remaining compounds of the series are by analogy regarded as monomers. Our interest in these complexes centered around their use as homogeneous hydrogenation and polymerization catalysts.

The complexes possess two properties which make their consideration as homogeneous catalysts attractive. (1) They are soluble in nonpolar or slightly polar,

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(1) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1343 (1963).

weakly basic solvents. (2) Since the titanium in the solution phase is only five-coordinate, the complexes possess at least one vacant coordination site, a condition deemed necessary for catalytic activity.[2]

Experimental Section

Materials.—Methylphosphine, dimethylphosphine, and trimethylphosphine were prepared according to the procedure of Jolly.[3] The samples were stored under vacuum at $-196°$ until used. Triethylphosphine (Pfaltz and Bauer) was stored under vacuum and transferred directly to the reaction vessel on the vacuum line. Titanium trichloride (Alfa Inorganics or K & K) was stored under argon, and all transfers of the solid were made in a glove bag under an argon atmosphere. Toluene (MCB) was distilled from phosphorus pentoxide and stored over sodium ribbon. Immediately prior to use, the solvent was degassed on the vacuum line.

Synthesis of $TiCl_3 \cdot 2PH_2(CH_3)$.—In a typical reaction, a 0.3366-g (2.18-mmol) sample of titanium trichloride was placed in a 25-ml reaction tube equipped with side-arm epr tube, visible cell, and glass break-seal. The apparatus was then attached to the vacuum line and evacuated for at least 1 hr. Approximately 7 ml of toluene was condensed into the reaction vessel followed by 4.40 mmol of methylphosphine, vp (vapor pressure) = 72 Torr ($-63°$) (73 Torr reported[3]). The reaction vessel was then sealed. After warming to room temperature, the mixture was placed in an oven held at 85° for 3–5 days. Filtration of the hot yellow-brown reaction solution into a side-arm tube of the reaction vessel followed by rapid cooling to room temperature gave dark red crystals, mp >275°. *Anal.* Calcd for $TiCl_3 \cdot 2PH_2(CH_3)$: C, 9.60; H, 4.03; Cl, 42.49. Found: C, 9.25; H, 4.15; Cl, 42.24.

Synthesis of $TiCl_3 \cdot 2PH(CH_3)_2$.—The procedure was essentially the same as that for the preparation of the methylphosphine adduct. A mixture of 0.1079 g (0.699 mmol) of titanium trichloride and 2.12 mmol of dimethylphosphine, vp = 34 Torr ($-45°$) (34 Torr reported[4]), in 8.6 ml of toluene was heated overnight at 85°. After the hot mixture was filtered into a side arm of the reaction vessel, a dark red-brown solid separated from the blue-green filtrate. Solvent and excess phosphine were removed from the reaction vessel under vacuum to give a red-brown solid, mp 177–189° dec. *Anal.* Calcd for $TiCl_3 \cdot 2PH(CH_3)_2$: C, 17.26; H, 5.07; Cl, 38.21; P, 22.25; Ti, 17.21. Found: C, 17.09; H, 5.28; Cl, 37.87; P, 21.98; Ti, 17.40.

Synthesis of $TiCl_3 \cdot 2P(CH_3)_3$.—Following the procedure described for the synthesis of the methylphosphine complex, 0.1060 g (0.689 mmol) of titanium trichloride was combined with 2.09 mmol of trimethylphosphine, vp = 49 Torr ($-45°$) (50 Torr reported[4]), in 7.7 ml of toluene. The mixture was held at 85° for 14 hr. The hot mixture was filtered into a side arm of the reaction tube. Removal of the solvent and excess phosphine from the yellow-brown filtrate gave a red-brown solid. The compound melts with decomposition over a temperature range of 230–255°. *Anal.* Calcd for $TiCl_3 \cdot 2P(CH_3)_3$: C, 23.52; H, 5.92; Cl, 34.71; P, 20.22; Ti, 15.63. Found: C, 23.35; H, 6.02; Cl, 34.89; P, 20.04; Ti, 15.52.

Synthesis of $TiCl_3 \cdot 2P(C_2H_5)_3$.—In the manner described above, a 0.1814-g (1.18-mmol) sample of titanium trichloride was combined with 0.60 ml (4.1 mmol) of triethylphosphine in 6.9 ml of toluene. After the mixture was heated at 85° for 15 min, the solution turned green-brown. Filtration of the mixture followed by evaporation of the filtrate to dryness gave a gray-green powder, mp 122.5–127.5°. *Anal.* Calcd for $TiCl_3 \cdot 2P(C_2H_5)_3$: C, 36.90; H, 7.74; Cl, 27.23; P, 15.86; Ti, 12.26. Found: C, 36.56; H, 7.81; Cl, 27.11; P, 15.55; Ti, 12.50.

Physical and Spectral Measurements.—Infrared spectral measurements were taken on a Beckman IR-10 spectrophotometer. The spectra were calibrated with polystyrene film. Band assignments are considered accurate to ± 5 cm^{-1}. The solids were mulled in a glove bag under an argon atmosphere, and the samples were placed between cesium bromide plates.

Visible spectra were taken on a Beckman DK-1A spectrophotometer using cells made of 1-cm² Pyrex tubing. The electron

resonance spectra were obtained with a Varian V4502-15 epr spectrometer.

The molecular weight of $TiCl_3 \cdot 2P(C_2H_5)_3$ in benzene was obtained by the freezing point depression method with an apparatus previously described.[5] The apparent molecular weight was 402 $\pm$ 14. The formula weight of $TiCl_3 \cdot 2P(C_2H_5)_3$ is 390.

Elemental analyses for the trimethylphosphine complex were carried out by Galbraith Laboratories, Knoxville, Tenn. All other elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany.

Results and Discussion

Despite variation of the phosphine:$TiCl_3$ mole ratio from 2 to 4 in the reaction mixtures, only the crystalline air-sensitive $TiCl_3 \cdot 2$(alkylphosphine) complexes were isolated. The epr spectra of toluene solutions containing 3 mol of phosphine per mole of titanium trichloride show a 1:3:3:1 quartet at $g = 1.94$ (Table I). Three

TABLE I
SUMMARY OF EPR DATA FOR TITANIUM(III) CHLORIDE–ALKYLPHOSPHINE ADDUCTS IN TOLUENE

Phosphine	Phosphine:TiCl₃ mole ratio	Temp, °C	g	a_p,[a] G	Shape
$(CH_3)PH_2$	3	-30	1.9427	25.84	1:3:3:1 quartet
$(CH_3)_2PH$	3	-20	1.9488	23.98	1:3:3:1 quartet
$(CH_3)_3P$	3	-20	1.9483	24.80	1:3:3:1 quartet
$(C_2H_5)_3P$	3	80	1.9626	22.82	1:2:1 triplet
		25	1.9626	22.82	1:2:1 triplet
		25	1.9432	25.30	1:3:3:1 quartet
		-20	1.9432	25.30	1:3:3:1 quartet

[a] Phosphorus coupling constant.

phosphine molecules appear to be associated with one titanium atom in the solution phase at -20 to $-30°$. The temperature dependence of the epr spectrum was tested in the case of the triethylphosphine adduct. Increasing the temperature from -20 to $+25°$ caused the appearance of a 1:2:1 triplet signal at $g = 1.96$ and a decrease in the intensity of the quartet signal. At a temperature of 80° only the triplet remains. An equilibrium

$$\Delta + TiCl_3[P(C_2H_5)_3]_3 = TiCl_3[P(C_2H_5)_3]_2 + P(C_2H_5)_3$$
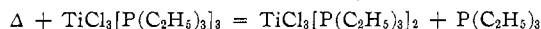
is indicated. The temperature dependence of the visible spectra of these reaction solutions is consistent with this interpretation. A solution of triethylphosphine and titanium trichloride showed bands at 470 and 610 nm of approximately equal intensity at 25°. Raising the temperature to 80° greatly increased the intensity of the band at 610 nm relative to the intensity of the 470-nm band. In addition, at room temperature it was found that the relative band intensity of $A_{470}:A_{610}$ increased as the $(C_2H_5)_3P$:$TiCl_3$ mole ratio was increased. The band at 610 nm is assigned to a d–d transition of a 2:1 complex while the 470-nm band is a d–d transition of the 3:1 complex. Table II provides a summary of visible spectra taken at room temperature of reaction mixtures containing 3:1 mole ratios of phosphine:$TiCl_3$.

Table III gives the tentative assignments of the major infrared absorption bands. Assignments of the

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alkylphosphine vibrations are based on data compiled by Corbridge[6] and by Beattie and Collis.[7] The Ti–P

TABLE II
SUMMARY OF VISIBLE SPECTRA FOR TITANIUM(III) CHLORIDE–ALKYLPHOSPHINE ADDUCTS IN TOLUENE AT ROOM TEMPERATURE

Phosphine	Phosphine: TiCl₃ mole ratio	Soln color	λ_1, nm	λ_2, nm
$(CH_3)PH_2$	3	Yellow-brown	497 ($\epsilon \sim 35$)	
$(CH_3)_2PH$	3	Blue-green	565[a]	660[a]
$(CH_3)_3P$	3	Yellow-brown	570[b]	650[b]
$(C_2H_5)_3P$	3	Green-brown	470[c]	610[c]

[a] Relative band intensity $A_{565}:A_{660} = 1.0$. [b] Relative band intensity $A_{570}:A_{650} = 1.2$–1.3. [c] Relative band intensity $A_{470}:A_{610} = 1.1$.

TABLE III
INFRARED SPECTRAL ASSIGNMENTS FOR TITANIUM(III) CHLORIDE–ALKYLPHOSPHINE ADDUCTS (CM⁻¹)

Assignment	$(CH_3)PH_2$	$(CH_3)_2PH$	$(CH_3)_3P$	$(C_2H_5)_3P$
C–H asym def	1415 m	1420 m	1425 s	1410 s
	1300 sh			
C–H sym def	1295 m	1298 m	1305 s	1270 m, br
	1265 m	1285 m	1290 s	
	1090 sh	1095 w	1090 w	1100 s, br
H–P–C def	1075 s			
CH₃ rock				1050 vs
	995 m	1000 sh		
H–P–C def		985 vs		
CH₃ rock	965 vs	955 vs	955 vs	965 m
	855 w	840 m	840 w	870 s, br
	805 w	790 w	785 w	
	755 w	745 m		
P–C str	720 s	730 m	735 s	765 vs, br
C–C str				740 sh
Ti–P str	410 s	375 vs	370 vs	320 vs
	400 s, sh			
Ti–Cl or Ti–P str	375 s	350 s	340 s	305 vs
Ti–Cl str	335 s	312 s	295 m	
	298 s			

stretching vibration for $TiCl_4 \cdot P(C_6H_5)_3$ was assigned to a 463-cm⁻¹ band.[8] This vibration occurs between 410 and 320 cm⁻¹ for the TiCl₃–alkylphosphine adducts. The frequency of the Ti–P stretch decreases as the size of the phosphine molecule increases. For each of the alkylphosphine complexes a second strong band 15–35 cm⁻¹ below the Ti–P stretch shows a similar decrease in frequency with increasing ligand size. This band is probably due to a complex Ti–Cl, Ti–P vibration. The methylphosphine adducts show a third band in the 335–295-cm⁻¹ region which is most probably a Ti–Cl stretching vibration.

An X-ray crystallographic study of single crystals of $TiCl_3 \cdot 2PH(CH_3)_2$ is in progress.

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Intramolecular Rearrangement Reactions of Tris(N-methyl-N-benzyldithiocarbamato)-iron(IV) Tetrafluoroborate by Proton Magnetic Resonance

BY D. J. DUFFY AND L. H. PIGNOLET*

The determination of mechanisms for intramolecular metal-centered rearrangement reactions of tris-chelate complexes has always been an important problem in inorganic chemistry.[1] Recent interest has been sparked by the use of dynamic nmr (dnmr) spectroscopy in the elucidation of such mechanisms. Several reviews of this topic have recently appeared.[2] The majority of the dnmr investigations have dealt with diamagnetic tris-bidentate-chelate complexes of trivalent metals such as Al, Ga, In, and Co.[3–9] In some of these cases mechanisms of isomerization reactions were sought by computer analysis of complex coalescence patterns.[3,5] The analyses were elegantly performed and in one case a unique mechanism was derived.[3] Paramagnetic complexes which manifest the isotropic shift phenomenon offer the added advantage of nonlinearly magnifying chemical shift differences between similar but magnetically nonequivalent nuclei.[10] Several dnmr investigations on paramagnetic tris-chelate systems have appeared[11–15] and in three cases mechanistic information was inferred.[11a,13,14] In these cases a computer analysis was unnecessary in determining the mechanism because all nonequivalent nuclei were resolved and the isomerization pathway was elucidated from the coalescence pattern alone.

We report here the first dnmr investigation of a tris-chelate complex of iron in the "IV" formal oxidation state: tris(N-methyl-N-benzyldithiocarbamato)-iron tetrafluoroborate, $[Fe(MeBz(dtc))_3]BF_4$ (I). This complex was prepared by air oxidation of Fe(MeBz(dtc))₃ (II) in the presence of BF_3. Pasek and Straub[16] recently reported this oxidation and characterized a series of compounds as cationic "iron(IV)"

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