quency in hexacarbonyls is about 0.25 eV.[27] However, such vibrational structure is weak in the CO molecule itself,[3] and since the added electron in the $Mo(CO)_6$ anion is distributed over six ligands, we would expect the C–O distance change to be smaller and the vibrational structure even weaker.

This assignment yields a plausible explanation for the energy trends along the series Cr, Mo, W for the intermediate energy peaks. Since the $8e_g$ orbital has some metal d character, we expect it to change in energy as M is changed. The separation of the metal d ligand field t_{2g} and e_g orbitals ($3t_{2g}$ and $7e_g$ in $Mo(CO)_6$) is calculated to increase from 4.6 eV in $Cr(CO)_6$ to 5.9 eV in $Mo(CO)_6$ so that the antibonding e_g orbitals are apparently destabilized along the series. The $3t_{2u}$ orbital on the other hand is essentially a CO orbital, correlating with the 2π. Experimental studies suggest that the M–C distance is shorter in $Cr(CO)_6$ than in $Mo(CO)_6$ or $W(CO)_6$ and that the C–O distance is longer.[20] A larger C–O separation would be consistent with a lower energy $3t_{2u}$ orbital in $Cr(CO)_6$.

It is difficult to obtain from theory an accurate quantitative comparison between $Mo(CO)_6$ and the other hexacarbonyls due to inevitable computational artifacts resulting from the choice of sphere radii and other effects. However, we have found that electron affinities calculated for $Cr(CO)_6$ by using a previously employed parameter set[11] and the same stabilization method employed for $Mo(CO)_6$ are −0.2, −1.7, and −2.8 for the orbitals corresponding to $7e_g$, $3t_{2u}$, and $8e_g$, respedtively. Thus, the antibonding ligand field orbital (the $7e_g$ analogue) is more stable by about 0.5 eV in the Cr compound, and the analogue of the $3t_{2u}$ orbital is more stable by about 0.6 eV. The $8e_g$ analogue, however, is unchanged in energy. Although the electron attachment transition state has not been studied for the $Cr(CO)_6$ analogue of the $6t_{2g}$ orbital, its approximate ground-state orbital energy suggests that it is stabilized by about 0.7 eV in the Cr case as observed.

Our analysis therefore suggests that the d^6 transition-metal hexacarbonyls have a number of stable negative ions obtained from population of orbitals correlating with the 2π of CO. The lowest energy unstable negative ions arise from occupation of the e_g ligand field orbital, the highest energy 2π-type orbitals, and the 6σ-type orbitals. The scattered-wave $X\alpha$ method with a stabilizing Watson sphere yields electron affinities qualitatively consistent with those observed. In vieew of our results it is surprising that stable anions of these compounds have not been observed in solution although it is possible the hexacarbonyl anions give up CO to form a stable pentacarbonyl anion similar to the behavior of $Fe(CO)_5$ and $Ni(CO)_4$ upon electron capture.[28]

In summary then, we have made the first measurements of the energies of negative ion states of transition-metal complexes. We have in addition demonstrated that plausible state assignments can be made on the basis of SCF $X\alpha$ calculations employing the transition-state procedure to get electron affinities associated with electron capture into orbitals whose energies are obtained by means of a stabilization method.

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(27) Hawkins, N. J.; Mattraw, H. C.; Sabol, W. W.; Carpenter, D. R. *J. Chem. Phys.* **1955**, *23*, 2422.

(28) Compton, R. N.; Stockdale, J. A. D. *Int. J. Mass. Spectrom. Ion. Phys.* **1976**, *22*, 47.

^{31}P NMR Spectra of Chelated (Diphosphine)rhodium Complexes in Solution

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Abstract: The $^{31}P\{^1H\}$ FT NMR spectra of Rh complexes that form in solution via ligand exchange of diphosphines with $HRh(CO)(PPh_3)_3$ have been scanned in order to characterize the complexes that form since with certain diphosphines such solutions catalyze selective olefin hydroformylation. It is shown that these diphosphines readily form Rh complexes under NMR conditions that exhibit 16-line multiplet spectra. The multiplets were simulated with AB_2X and ABCX (A, B, C = ^{31}P, X = ^{103}Rh) models and are attributed to approximately trigonal-bipyramid complexes of formula $HRh(CO)(P{\sim}P)(PR_3)$, $[HRh(CO)(P{\sim}P)_{1.5}]_2$, and $HRh(CO)(P{\sim}P)(P{\sim}P)^m$, where R = PPh_3 or $PEtPh_2$, m = monodentate, and P∼P = certain diphosphines including [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(diphenylphosphine), diop, *trans*-1,2-bis((diphenylphosphino)methyl)cyclobutane, *t*-bdcb, 1,1′-bis(diphenylphosphino)ferrocene, fdpp-1, and 1,1′-bis(bis(*p*-(trifluoromethyl)phenyl)phosphino)ferrocene, fdpp-2.

The complex $HRh(CO)(PPh_3)_3$ (**1**) is a well-known active catalyst for olefin hydroformylation.[1] In the presence of large excess concentrations of PPh_3 and under specific reaction conditions **1** confers a high selectivity in the conversion of α-olefins to linear (vs. branched) aldehydes.

It was recently shown[2] that certain diphosphines including *trans*-1,2-bis((diphenylphosphino)methyl)cyclobutane, *t*-bdcb, [(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis(di-

(1) (a) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1–60. (b) Paulik, F. E. *Catal. Rev.* **1972**, *6*, 49–84.

(2) (a) Unruh, J. D.; Christenson, J. R., submitted for publication in *J. Mol. Catal.* (b) Hughes, O. R.; Unruh, J. D., submitted for publication in *J. Mol. Catal.* **1981**, *12*, 71–83.

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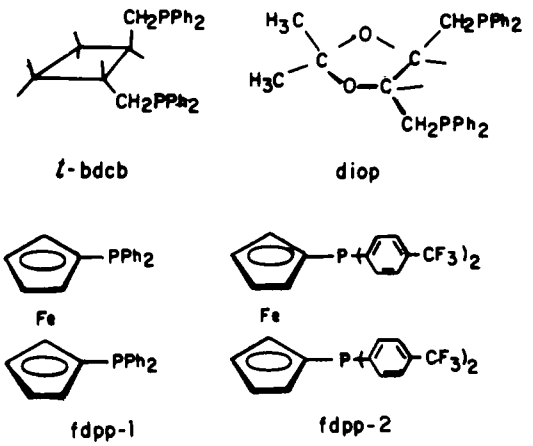
Table I. Solution Compositions

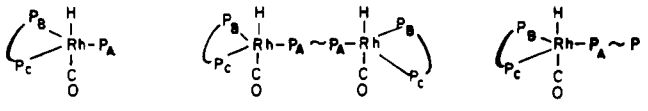
soln	P~P	[P~P][a]	addl PR_3	$[PR_3]$[a]	$[HRh(CO)(PPh_3)_3]$[a]	P~P:Rh	PR_3:Rh
1a	*t*-bdcb	0.017			0.036	0.48	
b		0.043			0.043	0.99	
c		0.14			0.027	5.0	
d		0.043	PPh_3	0.23	0.043	1.0	5.3
e		0.043	$PEtPh_2$	0.26	0.043	1.0	6.0
f		0.043	$P(i\text{-}Bu)_3$	0.25	0.043	1.0	5.8
2a	(+)-diop	0.05			0.050	1.0	
b		0.25			0.050	5.0	
c		1.0			0.050	20	
3a	fdpp-1	0.025			0.050	0.50	
b		0.050	$PEtPh_2$	0.25	0.050	1.0	5.0
4a	fdpp-2	0.0056			0.012	0.47	
b		0.012			0.012	1.0	
c		0.024			0.012	2.0	
d		0.060			0.012	5.0	
5a	dppp	0.017			0.036	0.48	
b		0.060			0.040	1.5	
c		0.14			0.027	5.0	
6a	dppb	0.014			0.029	0.50	
b		0.038			0.025	1.5	
c		0.13			0.027	4.9	

[a] Initial molar concentration.

phenylphosphine), diop, 1,1′-bis(diphenylphosphino)ferrocene, fdpp-1, and 1,1′-bis(bis(*p*-(trifluoromethyl)phenyl)phosphino)-ferrocene, fdpp-2 combine with Rh source complexes (including **1**) to form active catalysts for olefin hydroformylation. Solutions



of these diphosphines unlike solutions of simple methylene-bridged diphosphines (i.e., $Ph_2P(-CH_2)_nPPh_2$, n = 2–4, dppe, dppp, and dppb, respectively) with Rh source complexes confer sharply higher linear aldehyde selectivities when the diphosphine (P~P):Rh ratio is 1.5:1 or greater. At lower P~P:Rh ratio (i.e., 1:1) the selectivity of 1-hexene hydroformylation is sensitive to the nature and size of monophosphines when these are added. These observations imply that to be selective to linear aldehydes in hydroformylation a Rh complex must have three phosphine ligands coordinated at the instant that selectivity is determined. The special diphosphines confer higher selectivities because they form more stable, chelate complexes and thereby increase the likelihood that complexes having three coordinated phosphine groups will exist under reaction conditions. Complexes **2a**, **3**, and **4** were postulated to account



for the higher selectivities observed. In the work reported here $^{31}P\{^1H\}$ FT NMR is used to characterize the geometry and types of complexes that form when diphosphines combine with **1** via ligand exchange in order to provide evidence for the source of the hydroformylation selectivity of these solutions.

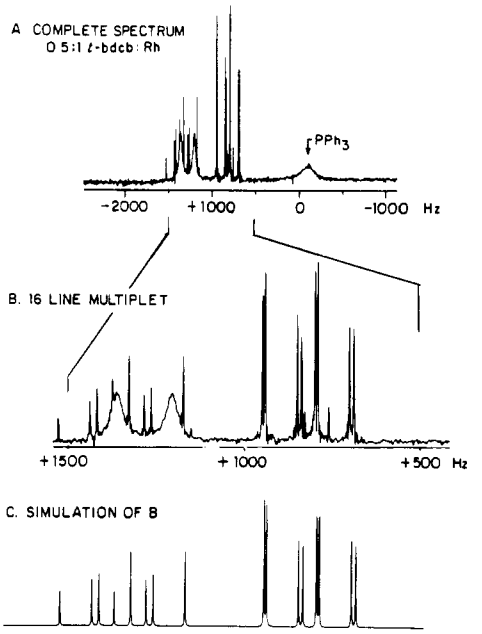


Figure 1. Comparison of the observed and simulated $^{31}P\{^1H\}$ FT NMR spectra of a solution of $HRh(CO)(PPh_3)_3$ in toluene to which *t*-bdcb has been added to achieve a 0.5:1 *t*-bdcb:Rh ratio (solution 1a). A and B are observed spectra; C is a simulation of B using the AB_2X model.

Experimental Section

$^{31}P\{^1H\}$ FT NMR. The ^{31}P NMR spectra were recorded with a Varian CFT-20 Fourier transform spectrometer equipped with a ^{31}P probe operating at 32.2 MHz. The spectra were scanned at 37 °C in the proton-decoupled mode with a pulse angle of 40° (4 μs) and an accumulation time of 0.50 μs. The spectrometer was referenced to 85% H_3PO_4 in an 8-mm NMR tube. Shifts to high field are negative. Sample spectra were subsequently accumulated by using a benzene-d_6 lock sample in a sealed capillary tube in the 8-mm NMR sample tube. Total accumulation times ranged from 2 to 16 h. Low-temperature spectra were recorded by using an acetone-d_6 lock capillary.

The spectra were simulated with a Nicolet 1180 computer (Nicolet Instrument Corp., Madison, WI) and the Nicolet ITRCAL (LAOCN3-based) iterative program.

Samples. The preparation of **1** and the diphosphines (*t*-bdcb, fdpp-1, fdpp-2) were described previously.[2] (+)-Diop was purchased from Strem Chemicals, Inc., Newburyport, MA, and used without further purification. The solution samples were prepared in a N_2 box from stock solution

Table II. 16-Line Multiplet Parameters

soln	model[a]	δ_A[b]	δ_B	δ_C	J_{Rh-P_A}[c]	J_{Rh-P_B}	J_{Rh-P_C}[d]	$J_{P_A-P_B}$	$J_{P_A-P_C}$	error[b]
1a	B2	41.57	25.61		154	149		101		0.0092
	BC	41.57	25.64	25.59	154	148	150	110	92.7	0.0079
1b	B2	41.27	25.61		154	150		102		0.0241
	BC	41.27	25.85	25.36	154	155	144	110	93.5	0.0093
1c	B2	29.44	25.82		151	146		104		0.0155
1d	B2	41.61	25.68		153	149		101		0.0061
	BC	41.61	25.58	25.78	153	151	147	95.6	107	0.0081
1e	B2	33.90	25.85		151	146		99.5		0.0129
	BC	33.90	25.76	25.94	151	137	155	102	97.6	0.0077
1f	B2	41.55	25.59		154	149		101		0.0119
	BC	41.55	25.63	25.55	154	150	148	99.2	102	0.0120
2a	B2	41.23	20.25		152	149		96.9		0.0412
	BC	41.21	20.38	20.14	152	150	149	127	67.0	0.0086
2c	B2	29.95	20.61		152	145		95.6		0.0350
	BC	29.92	20.76	20.50	152	149	144	117	73.6	0.0072
3a	B2	39.97	30.29		159	155		124		0.0119
	BC	39.97	30.26	30.31	159	149	161	119	148	0.0107
3b	B2	33.73	30.20		156	152		128		0.0100
	BC	33.73	30.23	30.17	156	154	150	129	127	
4c	B2	41.81	30.93		157	155		124		
5c	B2	26.69	17.90		143	126		53.8		0.0106
	BC	26.69	17.84	17.97	143	129	123	57.2	50.4	0.0102

[a] B2 = AB_2X model. BC = ABCX model. [b] Ppm. [c] Hertz. [d] $J_{P_B-P_C}$ arbitrarily set equal to 128.8 Hz.

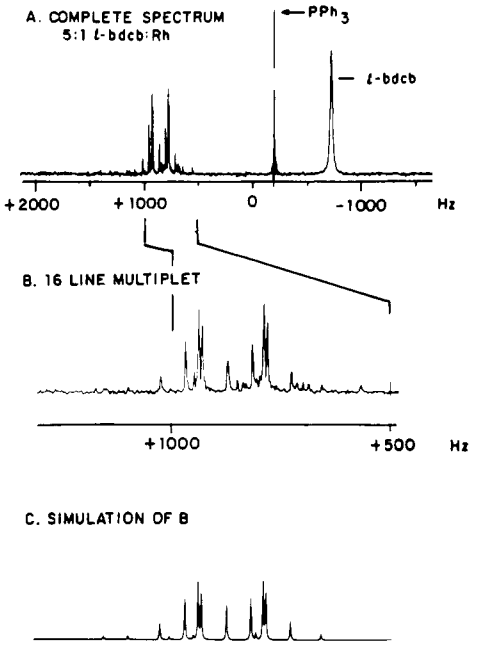


Figure 2. Comparison of the observed and simulated $^{31}P\{^1H\}$ FT NMR spectra of a solution of $HRh(CO)(PPh_3)_3$ in toluene to which *t*-bdcb has been added to achieve a 5:1 *t*-bdcb:Rh ratio (solution 1c). A and B are observed spectra, C is a simulation of B using the AB_2X model.

by using dilution techniques. Solutions that were sealed under N_2 were stable for long periods.

Results

Table I is a tabulation of solution compositions that were examined by $^{31}P\{^1H\}$ FT NMR. These solutions were formed to provide series in which the ratio of each diphosphine to **1** is varied from 0.5:1 to 20:1. The spectra in Figures 1 through 3 are typical. Many of the spectra have a 16-line multiplet component that originates in a 4-spin ($^1/_2$) system which could be simulated by using an ABCX (i.e., $P_AP_BP_CRh$) or AB_2X (i.e., P_A2P_BRh) models. Both ^{31}P and ^{103}Rh are 100% abundant spin $^1/_2$ nuclei. The multiplet parameters that produced the lowest residual error in the simulation are tabulated in Table II.

In most cases a slightly lower residual error was achieved with the ABCX model. But in every case the best-fit parameters for P_B and P_C (i.e., δ_{P_B}, δ_{P_C}, J_{Rh-P_B}, J_{Rh-P_C}, $J_{P_A-P_B}$, $J_{P_A-P_C}$) differ little from, and average to, the parameters for P_B (δ_{P_B}, J_{Rh-P_B}, $J_{P_A-P_B}$)

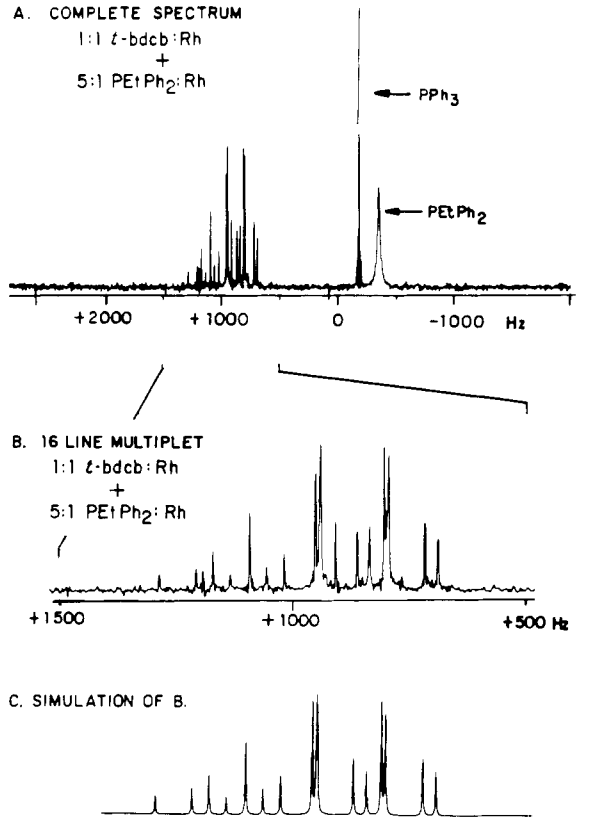


Figure 3. The $^{31}P\{^1H\}$ FT NMR spectrum of a solution of $HRh(CO)(PPh_3)_3$ in toluene to which *t*-bdcb and $PEtPh_2$ have been added to achieve the indicated ratios (solution 1e). A and B are observed spectra, C is a simulation of B using the AB_2X model.

in the AB_2X model. The greatest difference in P_B and P_C parameters occurs in the $J_{P_A-P_B}$ vs. $J_{P_A-P_C}$ values. Forced changes in these coupling constants have little effect on the resulting residual error so the fact that the best-fit constants differ is not viewed as evidence that P_B and P_C are coordinated in nonequivalent sites. The lower residual error achieved with the ABCX model is attributed to the fact that three additional independent variables are used in the simulation. Thus the AB_2X model in which P_B and P_C are magnetically equivalent is adequate and preferred.

***t*-bdcb.** At 0.5:1 *t*-bdcb:Rh (solution 1a) the spectrum (Figure 1) contains contributions from (1) the broadened doublet of **1** (δ

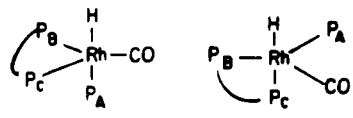
39.79 (J_{Rh-P} = 159.4 Hz)), (2) a sharp 16-line multiplet, and (3) a broadened singlet (δ −3.23 (half-bandwidth = 80 Hz)) due to displaced PPh_3. The multiplet was simulated with AB_2X and ABCX models with the parameters in 1a (Table II). P_B and P_C are attributed to PPh_2CH_2 groups in *t*-bdcb that is chelated in nearly equivalent sites. If it is assumed that a trigonal-bipyramidal (tbp) structure, perhaps distorted, is retained during ligand exchange, the nearly equivalent sites to which P_B and P_C are coordinated must be equatorial sites in the tbp.

P_A in 1a is attributed to PPh_3. This is likely since at low *t*-bdcb:Rh ratios there is not sufficient *t*-bdcb to displace PPh_3 completely. P_A is apparently coordinated in an equatorial site of the tbp since δ_A (41.57) is close to the δ of PPh_3 in **1** (39.79) where it is known to be coordinated in an equatorial site of a distorted tbp.

In summary, the multiplet in the spectrum of 1a is attributed to HRh(CO)(*t*-bdcb)(PPh_3) with structure **2a** (P_A = PPh_3) which is formed from **1** by the ligand-exchange reaction (1). Of the

$$HRh(CO)(PPh_3)_3 \underset{PPh_3}{\overset{P\sim P}{\rightleftharpoons}} HRh(CO)(P\sim P)(PPh_3) \quad (1)$$

alternative tbp structures (**2b**, **2c**) for HRh(CO)(*t*-bdcb)(PPh_3)



2b **2c**

2b is unlikely since it appears that three large phosphine ligands are better accommodated in the equatorial sites in tbp HRh(CO)(PR_3)$_3$ complexes. This is supported by the X-ray structure of **1** in which each of three PPh_3 ligands are assigned equatorial sites.[3]

A rigid structure **2c** in which the diphosphine would span axial and equatorial coordination sites is ruled out for the reason that in **2c** P_B and P_C are required to be coordinated in magnetically nonequivalent sites. This requires a larger difference in δ_B and δ_C and in J_{Rh-P_B} and J_{Rh-P_C} than is observed. In the ABCX simulation of the multiplet in the spectrum of solution 1a, δ_B and δ_C differ by only 0.05 ppm and J_{Rh-P_B} and J_{Rh-P_C} differ by only 2 Hz. In several of the well-characterized comparisons that have been reported[4] $J_{Rh-P_{eq}}$ is 30–57 Hz larger than $J_{Rh-P_{ax}}$.

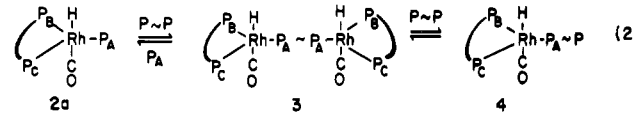
If P_B and P_C are magnetically equivalent, as it is asserted here, then $J_{P_A-P_B}$ and $J_{P_A-P_C}$ should be equivalent. However, the ABCX simulation of the solution 1a spectrum gave best-fitting $J_{P_A-P_B}$ and $J_{P_A-P_C}$ constants which differed (110 and 92.7 Hz, respectively). In fact this difference is not important in reducing the error of the simulation and is likely not physically significant.

An AB_2X multiplet could arise from a fluxional **2c** structure in which P_B and P_C are rapidly equilibrated. In such a case P_B and P_C would exhibit equivalent, averaged spectral features. Variable-temperature NMR studies did not provide evidence for such fluxionality (see below). A similar multiplet was retained at temperatures as low as 189 K, indicating that the hypothetical fluxionality could not be frozen-out at these temperatures.

At 1:1 *t*-bdcb:Rh (solution 1b) the spectrum (not shown) is similar to that of the 0.5:1 solution except that the doublet for unconverted **1** is absent and the singlet (δ −4.20 (half-bandwidth = 40 Hz)) for displaced PPh_3 is shifted closer to the position of neat PPh_3 and is sharpened somewhat.

At 5:1 *t*-bdcb:Rh (solution 1c) the spectrum (Figure 2) consists of (1) a new 16-line multiplet, (2) a sharp singlet (δ 5.80 (half-bandwidth < 5 Hz)) for free displaced PPh_3, and (3) a broadened singlet (δ −22.07 (half-bandwidth = 10 Hz)) for free excess *t*-bdcb. The new multiplet was simulated with the AB_2X model. δ_B in 1c is similar to δ_B and δ_C in 1a and 1b and is therefore attributed to PPh_2CH_2– in *t*-bdcb that is chelated to equivalent equatorial tbp sites. The chemical shift of P_A in solution 1c (δ_A 29.44) is at higher field than that of P_A in 1a or 1b (δ_A 41.57 and 41.27, respectively) and is close to the value of PPh_2CH_2– in chelated *t*-bdcb (δ_B 25.82 in solution 1c). P_A in 1c is therefore attributed to PPh_2CH_2– in *t*-bdcb which is coordinated as a monodentate ligand.

In summary, the multiplet in solution 1c is attributed to HRh(CO)(*t*-bdcb)(*t*-bdcb)^m (where m signifies that the diphosphine is coordinated as a monodentate ligand) with rigid structure **4** or a fluxional structure **2c** formed in the ligand-exchange reaction (2) (exemplified with **4** only). Since the chemical



2a **3** **4** (2)

shift of uncoordinated PPh_2CH_2 group in monodentate *t*-bdcb is not distinguishable from that of free *t*-bdcb, the contribution, if any, of a dinuclear species **3** cannot be assessed.

In the 1d solution additional PPh_3 was added to a solution containing HRh(CO)(*t*-bdcb)(PPh_3). The resulting spectrum was identical with that of HRh(CO)(*t*-bdcb)(PPh_3) in 1b except that the PPh_3 singlet was more intense, sharper (half-bandwidth = 20 Hz) and shifted (δ −5.85) closer to the value of neat PPh_3. Thus the additional PPh_3 had no effect on the multiplet for HRh(CO)(*t*-bdcb)(PPh_3).

In the 1e solution $PEtPh_2$ was added to a solution containing HRh(CO)(*t*-bdcb)(PPh_3) to form a solution having $PEtPh_2$:*t*-bdcb:PPh_3:Rh in 5:1:3:1 ratio. The resulting spectrum (Figure 3) consisted of (1) a 16-line multiplet, (2) a sharp singlet (δ −5.80 (half-bandwidth = <5 Hz)) for displaced PPh_3, and (3) a broadened singlet (δ −11.07 (half-bandwidth = 35 Hz)) for excess $PEtPh_2$. δ_B and δ_C in 1e are similar to δ_B and δ_C in the other complexes having chelated *t*-bdcb and are attributed to PPh_2CH_2– from that source here as well.

The chemical shift and coupling constant of P_A in 1e (δ_A 33.90 (J_{Rh-P} = 151 Hz)) is significantly different than that of P_A in 1a (δ_A 41.57) where it is attributed to PPh_3 and different than that of P_A in 1c (δ_A 29.44) where it is attributed to PPh_2CH_2– but is close to the shift of $PEtPh_2$ in HRh(CO)($PEtPh_2$)$_3$.[5] Hence P_A in 1c is attributed to $PEtPh_2$ coordinated in an equatorial site.

In summary, the multiplet in 1e is attributed to HRh(CO)(*t*-bdcb)($PEtPh_2$) with structure **2a** (**2c**, if fluxionality is assumed) which is formed via the ligand-exchange reaction (3).

$$HRh(CO)(P\sim P)(PPh_3) \underset{PPh_3}{\overset{PEtPh_2}{\rightleftharpoons}} HRh(CO)(P\sim P)(PEtPh_2) \quad (3)$$

In the 1f solution P(*i*-Bu)$_3$ was added to a solution containing HRh(CO)(*t*-bdcb)(PPh_3) which was formed by adding *t*-bdcb to a solution of HRh(CO)(PPh_3)$_3$. The resulting solution had a P(*i*-Bu)$_3$:*t*-bdcb:PPh_3:Rh ratio of 5.8:1:3:1 and a spectrum consisting of (1) at 16-line multiplet, (2) a sharp singlet (δ −5.88) for displaced PPh_3, and (3) a sharp singlet (δ −25.06) for P(*i*-Bu)$_3$. The multiplet was simulated with equal success by using AB_2X or ABCX models. The resulting δ and J parameters (Table II, solution 1f) are similar to those used to model the spectra of solutions 1a and 1d that contain HRh(CO)(*t*-bdcb)(PPh_3). It is concluded that the multiplet emminates from HRh(CO)(*t*-bdcb)(PPh_3) in solution 1f as well. P(*i*-Bu)$_3$ did not displace PPh_3 in this instance.

(3) LaPlaca, S. J.; Ibers. J. A. *J. Am. Chem. Soc.* **1963**, *85*, 3501.

(4) (a) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120. (b) Garrou, P. E.; Curtis, J. L. S.; Hartwell, G. E. *Inorg. Chem.* **1976**, *15* (12), 3094. (c) Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95* (22), 7272. (d) Tiethof, J. A.; Peterson, J. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15* (6), 1365.

(5) HRh(CO)($PEtPh_2$)$_3$ was generated in toluene solution from 0.027 M HRh(CO)(PPh_3)$_3$ by adding $PEtPh_2$ to a concentration of 0.133 M to achieve a 5:1 $PEtPh_2$:Rh ratio. The $^{31}P\{^1H\}$ FT NMR spectrum consisted in (1) a broadened doublet (δ 32.58 (J_{Rh-P} = 170.2 Hz, half-bandwidth = ~30 Hz)) attributed to HRh(CO)($PEtPh_2$)$_3$, (2) a slightly broadened singlet (δ −5.60 (half-bandwidth = ~12 Hz)) attributed to displaced PPh_3, and (3) a broadened singlet (δ −10.88 (half-bandwidth = ~43 Hz)) attributed to excess, uncoordinated $PEtPh_2$.

Table III. FT IR Stretching Frequencies (cm^{-1})[a]

	ν_{Rh-H}	ν_{Rh-D}	ν_{CO}
1[b]	2008		1927
$DRh(CO)(PPh_3)_3$		c	1965
1[b] + 0.04 M (+)-diop	2001		1927
1[b] + 0.04 M (+)-diop + D_2[d]		c	1963
$DRh(CO)(PPh_3)_3$[e] + 0.04 M (+)-diop		c	1968
$DRh(CO)(PPh_3)_3$[e] + 0.08 M (+)-diop		c	1966

[a] 0.0250-cm cell path, 25 °C, toluene spectrum subtracted. [b] 0.02 M in toluene solution. [c] ν_{Rh-D} not observed due to solvent and ligand interference. [d] Gently sparging at 1 atm, 25 °C, 20 min. [e] 0.02 M in toluene, from $(PPh_3)_2Rh(CO)Cl$ and $NaBD_4$.

diop. Solutions (2a–c, Table I) having 1:1, 5:1, and 20:1 diop:Rh ratios were scanned. The spectra were similar to those in Figures 1 and 2 and are therefore not shown.

The 1:1 diop:Rh solution spectrum (2a) consisted of (1) a 16-line multiplet and (2) a broadened singlet for displaced PPh_3. The multiplet which had an appearance similar to that for $HRh(CO)(t\text{-bdcb})(PPh_3)$ in Figure 1c was simulated with AB_2X and ABCX models (2a, Table II). P_B and P_C are attributed to PPh_2CH_2- in diop that is either (1) chelating equivalent equatorial sites in a rigid **2a** structure or (2) chelating nonequivalent axial–equatorial sites in a fluxional **2c** structure.

The chemical shift of PPh_2CH_2- in chelated diop (δ_B 20.38, δ_C 20.14) is at somewhat higher field than that of PPh_2CH_2- in chelated *t*-bdcb (δ_B 25.85, δ_C 25.36 in 1b) in the same environment.

The chemical shift of P_A in 2a (δ_A 41.21) is a value within the range of shifts observed for PPh_3 in equatorial sites and is attributed this significance in 2a.

In summary, the multiplet in solution 2a is attributed to $HRh(CO)(diop)(PPh_3)$ with a rigid structure **2a** (or a fluxional structure **2c**) formed via eq 1.

The 5:1 (2b) and 20:1 (2c) diop:Rh solution spectra each had (1) a 16-line multiplet, (2) a sharp singlet for displaced PPh_3, and (3) a singlet for free excess diop (δ −23.34). The multiplets in 2b and 2c were identical but different than the multiplet in 2a. P_B and P_C are attributed to the PPh_2CH_2- groups of chelated diop in a rigid **4** structure or a fluxional dinuclear equivalent of **2c**.

The chemical shift of P_A in 2c (δ_A 29.92) is significantly different than its value in 2a (δ_A 41.21) but close to its value (δ_A 29.44) in 1c where it is attributed to PPh_2CH_2- in *t*-bdcb coordinated as an equatorial monodentate ligand. P_A in 2c is therefore attributed to PPh_2CH_2- in diop coordinated as a monodentate ligand.

In summary the 2b and 2c multiplets are attributed $[HRh(CO)(diop)_{1.5}]_2$ with structure **3** or to $HRh(CO)(diop)(diop)^m$ with structure **4**.

The infrared spectra of solutions of **1** or $DRh(CO)(PPh_3)_3$ alone or with (+)-diop were examined because it has been shown[6] that ν_{CO} in a variety of metal–carbonyl hydride complexes is sensitive to the presence of H or D ligands if these are trans (but not if cis) to the CO ligand. Therefore, if diop reacts with **1** to form **2a**, **3**, or **4**, then ν_{CO} should be shifted in the corresponding deuteride because the CO ligand is trans to H or D in these structures. If structure **2b** or **2c** forms, no shift in ν_{CO} on comparing corresponding hydride and deuteride spectra is expected.

The ν_{RhH} and ν_{CO} which originate in solutions of (+)-diop and Rh source complexes are listed in Table III. In the solutions that contain diop, the diop:Rh ratios are intermediate between the ratios in solutions 2a and 2b in Table I which were examined by ^{31}P NMR. Therefore $HRh(CO)(diop)(PPh_3)$, $[HRh(CO)(diop)_{1.5}]_2$, and $HRh(CO)(diop)(diop)^m$ or the corresponding deuterides are present.

It can be seen that ν_{Rh-H} and ν_{CO} for the solution of **1** alone or with diop are similar and ν_{CO} for the solution of $DRh(CO)(PPh_3)_3$ alone or with diop are similar. These stretching frequencies are insensitive to the nature of the phosphine ligands in the complex.

(6) Vaska, L. *J. Am. Chem. Soc.* **1968**, *88* (*17*), 4100.

However, the solutions having carbonyl and hydride ligands have ν_{CO} = 1927 cm^{-1} while solutions with carbonyl and deuteride ligands have ν_{CO} = 1963–1968 cm^{-1}. This is a shift of ν_{CO} of the magnitude and direction that is expected if the CO ligand is trans to the hydride (deuteride) ligand. The IR and ^{31}P NMR work support the same conclusion, i.e., that structures **2a**, **3**, and **4** with the CO ligand trans to H are preferred over structures **2b** or **2c**.

fdpp-1. The spectrum of a solution of fdpp-1 and **1** in 0.5:1 ratio (3a) consisted of (1) a broadened doublet (δ 39.97 (J_{Rh-P} = 159.4 Hz)) for unreacted **1**, (2) a broadened singlet (δ −3.91) for displaced PPh_3, and (3) a sharp 16-line multiplet which was simulated with AB_2X and ABCX models with the parameters in 3a of Table II. P_B and P_C are attributed to PPh_2Cp- groups in fdpp-1. P_A has a chemical shift (δ_A 39.97) that falls in the range of values for PPh_3 coordinated to Rh in the equatorial plane of a tbp complex and is assigned that significance in 3a. The 3a multiplet is therefore attributable to $HRh(CO)(fdpp\text{-}1)PPh_3$ with a rigid **2a** structure (or a fluxional **2c** structure) which is formed via eq 1.

In 3b $PEtPh_2$ was added to a solution containing $HRh(CO)(fdpp\text{-}1)PPh_3$ to form a solution having fdpp-1:$PEtPh_2$:Rh in 1:5:1 ratio. The spectrum consisted of (1) a sharp singlet (δ −5.80) for displaced PPh_3, (2) a broadened singlet (δ −11.07) for free excess $PEtPh_2$, and (3) a 16-line multiplet. The multiplet was simulated with AB_2X and ABCX models with the parameters in 3b of Table II. P_B and P_C are nearly equivalent in 3b and have chemical shifts similar to P_B and P_C in 3a where they were attributed to PPh_2Cp- in chelated fdpp-1. Thus P_B and P_C are assigned the same significance in the 3b multiplet. P_A in 3b has a chemical shift (δ_A 33.73) similar to that previously assigned to $PEtPh_2$ (δ_A in 1e equals 33.90). Hence the multiplet in 3b is attributed to $HRh(CO)(fdpp\text{-}1)(PEtPh_2)$ with a rigid **2a** structure (or a fluxional **2c** structure) which is formed via eq 3.

fdpp-2. Solutions (4a–d, Table I) having fdpp-2 and **1** in 0.5:1 through 5:1 ratios were formed and scanned. Identical 16-line multiplets were observed in each solution. The multiplet in solution in 4c was simulated with AB_2X and ABCX models with the parameters in 4c of Table II.

The 4a solution spectrum also had the broadened doublet for unreacted **1** (δ 39.95 (J_{Rh-P} = 159.7 Hz)).

The 4c and 4d solutions had broadened singlets for the displaced PPh_3 (δ −5.46 and −5.38, respectively) and for excess fdpp-2 (δ −17.95 and −17.91 vs. −17.97 for fdpp-2 alone in solution). The PPh_3 singlet did not sharpen at high fdpp-2:Rh ratios as it does in solutions with high *t*-bdcb or diop:Rh ratios, an indication of its continuing involvement in ligand-exchange equilibria. P_B (and P_C) in 4c has a chemical shift (δ 30.93) similar to that (δ 30.3) previously attributed to PPh_2Cp- in fdpp-1. In 4c P_B (and P_C) is attributed to $P(p\text{-}CF_3Ph)_2Cp-$ in fdpp-2. P_A in 4c has δ_A 41.81 which is consistent with an assignment of P_A as PPh_3 in an equatorial site. For these reasons and because the 16-line multiplet observed at low fdpp-2:Rh ratios persists at high fdpp-2:Rh ratios, the multiplet is attributed to $HRh(CO)(fdpp\text{-}2)(PPh_3)$ with a rigid **2a** structure (or a fluxional **2c** structure).

dppp. Solutions (5a–c Table I) having dppp and **1** in ratios of 0.5:1, 1.5:1, and 5:1, respectively, were examined.

The $^{31}P\{^1H\}$ NMR spectrum of the 5a solution consisted of (1) a broadened doublet for unreacted **1** (δ 39.84 (J_{Rh-P} = 151.7 Hz)), (2) a broadened singlet for displaced PPh_3 (δ −5.15), and (3) three unidentified doublets (1st, δ 21.94 (J_{Rh-P} = 161.6 Hz); 2nd, δ 20.64 (J_{Rh-P} = 132.0); 3rd, δ 18.59 (J_{Rh-P} = 133.0 Hz)).

The 5b solution consisted of (1) a 16-line multiplet, (2) two new doublets (4th, δ 17.62, (J_{Rh-P} = 141.7); 5th, δ 7.88 (J_{Rh-P} = 153.6)), and (3) a sharp singlet (δ −5.87) for displaced PPh_3.

The 5c solution consisted of (1) the same 16-line multiplet, (2) the fourth and fifth doublets at reduced intensity, (3) a sharp singlet (δ −5.87) for displaced PPh_3, and (4) a sharp singlet (δ −18.34) for uncoordinated excess dppp.

Table IV. Temperature Variation of Multiplet Parameters[a]

temp, K	δ_A	δ_B	J_{Rh-P_A}, Hz	J_{Rh-P_B}, Hz	$J_{P_A-P_B}$, Hz
310	41.80	30.92	157	155	124
248	43.75	31.92	156	156	122
189	45.10	32.54	156	156	121

[a] Solution 4c with an external acetone-d_6 capillary as lock.

The 16-line multiplet in 5c was simulated with AB_2X and ABCX models without significant difference in the residual error, hence P_B and P_C are attributed to PPh_2CH_2- in dppp chelated in equivalent sites. P_B (and P_C) has an average δ_B (and δ_C) value of 17.90 in 5c which is somewhat to higher field than δ for PPh_2CH_2- in chelated *t*-bdcb or diop. P_A has a chemical shift in 5c (δ_A 26.69) which is closer to that of PPh_2CH_2- in monodentate *t*-bdcb (29.44) and diop (29.92) than to PPh_3 (≈40).

In summary the multiplet in 5c is attributed to HRh(CO)(dppp)(dppp)[m] with structure **3** or **4**.

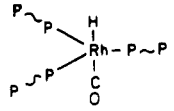
dppb. Solutions (6a–c, Table I) having dppb and **1** in 0.5:1, 1.5:1, and 5:1 ratios, respectively, were examined.

The spectrum of the 0.5:1 solution (6a) consisted of (1) a broadened doublet (δ 40.11 (J_{Rh-P} = 157.1 Hz)) for unreacted **1**, (2) a poorly resolved 16-line multiplet, and (3) a broadened singlet (δ −4.95) for displaced PPh_3.

The spectrum of the 1.5:1 solution (6b) consisted of (1) traces of the 16-line multiplet, (2) a sharp doublet (δ 31.14 (J_{Rh-P} 147.5 Hz)), (3) a broadened singlet (δ −5.81) for displaced PPh_3, and (4) a broadened singlet (δ −16.68) for excess dppb.

The spectrum of the 5:1 solution (6c) consisted of (1) the doublet, (2) a sharp singlet (δ −5.88) for displaced PPh_3, and (3) a sharp singlet (δ −16.99) for excess dppb.

The 16-line multiplet in 6a appears to be due to HRh(CO)(dppb)(PPh_3), but the multiplet was not sufficiently prominent to simulate. At higher dppb:Rh ratios the 16-line multiplet is replaced by the sharp doublet which is presumed to be HRh(CO)(dppb)$_3$ wherein each dppb ligand functions as a monodentate ligand, i.e., structure **5**. The chemical shift and Rh–P coupling



5

constant values of the doublet in 6b,c are similar to the values of the doublet observed for $PEtPh_2$ in HRh(CO)($PEtPh_2$)$_3$.[5]

Low-Temperature Spectra. The $^{31}P\{^1H\}$ NMR spectra of solution 4c (containing HRh(CO)(fdpp-2)(PPh_3)) was scanned at several temperatures over the range 189–337 K. Similar 16-line multiplets were observed at each temperature. Several of the multiplets could be simulated (AB_2X model) with the parameters in Table IV. The fact that the multiplet is retained at temperatures down to 189 K suggests that the complex is not fluxional. The fact that the multiplet can be adequately simulated with an AB_2X model and the indication that the complex is rigid lead to the conclusion that the complex is approximately trigonal bipyramidal as in **2a** (P_C = P_B).

However, the possibility exists that the complex is fluxional and that it can only be frozen out at temperatures below those investigated in this work (i.e., <189 K). If so the P_B and P_C nuclei would appear to be magnetically equivalent through $P_B \rightleftharpoons P_C$ scrambling yet could be coordinated in nonequivalent sites as in structure **2c**.

Although similar in appearance, none of the multiplets are superimposable. Both δ_A and δ_B shift to lower field at lower temperature. This accounts for a visible difference in the multiplets. The temperature dependences are approximately linear: $\Delta\delta_A/\Delta T$ = −0.027 ppm/K, $\Delta\delta_B/\Delta T$ = −0.013 ppm/K ± 0.002 ppm/K. Temperature dependences of this magnitude have been noted before[7] for free trivalent phosphorus compounds. This is the first observance that the phenomenon extends to phosphines coordinated in transition-metal complexes. The J_{Rh-P} and J_{P-P} coupling constants are not affected by the temperature variation.

Discussion

It is concluded that **1** can be readily and completely converted through ligand exchange with *t*-bdcb, diop, fdpp-1, and fdpp-2 to diphosphine complexes of structure **2**, **3**, or **4** (at room temperature under N_2). At low P∼P:Rh ratios (i.e., <1.5:1) an intermediate exchange product, HRh(CO)(P–P)(PPh_3), with a 1:1 P∼P:Rh ratio forms. These 1:1 complexes can undergo ligand exchange of the remaining PPh_3 ligand for a more strongly coordinating ligand (e.g., $PEtPh_2$) to form HRh(CO)(P∼P)($PEtPh_2$). Alternatively at higher (≥1.5:1) P∼P:Rh ratios the remaining PPh_3 can be exchanged for a second diphosphine.

The solution structures and exchange dynamics which are observed here under NMR conditions are believed to prevail under hydroformylation conditions (793 kPa, 1:1 H_2:CO, 110 °C) as well. The sharp increase in hydroformylation selectivity to linear aldehyde[2a] that certain diphosphines (*t*-bdcb, fdpp-1, etc.) confer at ≥1.5:1 P∼P:Rh has been attributed to the formation of complexes of structure **3** or **4** under hydroformylation conditions.

The lower linear aldehyde selectivity that the same diphosphines confer at <1.5:1 P∼P:Rh ratios is attributable to the predominance in solution of HRh(CO)(P∼P)(PPh_3) and to HRh(CO)$_2$(P∼P) which may form under hydroformylation conditions via eq 4.

$$HRh(CO)(P\sim P)(PPh_3) \underset{PPh_3}{\overset{CO}{\rightleftharpoons}} HRh(CO)_2(P\sim P) \quad (4)$$

Selective hydroformylation is also conferred when the same diphosphines are present at only 1:1 P∼P:Rh ratio if a monophosphine (e.g., $PEtPh_2$) is present as well.[2b] This is attributable to the formation of **2a** (P_A = $PEtPh_2$) under hydroformylation conditions just as it is observed to be formed under NMR conditions.

In a few instances the species observed under NMR conditions do not correspond to the species thought to be present under hydroformylation conditions. For example the 16-line multiplet for the complex that forms when P(*i*-Bu)$_3$ and *t*-bdcb are added to HRh(CO)(PPh_3)$_3$ (solution 1f, Table I) was simulated (1f, Table II) and found to be identical with the multiplet observed (1a, Table II) when HRh(CO)(*t*-bdcb)(PPh_3) was present. Hence the small excess P(*i*-Bu)$_3$ concentration (i.e., 5.8:1 P(*i*-Bu)$_3$:Rh) appears not to have sufficient to displace a significant amount of PPh_3 to form HRh(CO)(*t*-bdcb)(P(*i*-Bu)$_3$) under NMR conditions. Yet under hydroformylation conditions[2b] a similar small excess (10:1 P(*i*-Bu)$_3$:Rh, 1:1 *t*-bdcb:Rh) confers a distinctly higher selectivity to linear aldehyde than does PPh_3, implying that HRh(CO)(*t*-bdcb)(P(*i*-Bu)$_3$) does form under reaction conditions.

In the case of the weakly coordinating diphosphine, fdpp-2, the final PPh_3 is not readily displaced by fdpp-2 so that HRh(CO)(fdpp-2)(PPh_3) is observed rather than complexes with structure **3** or **4** at fdpp-2:Rh ratios to 5:1. Under hydroformylation conditions,[2a] however, the final PPh_3 is thought to be displaced to yield complexes with structure **3** or **4**.

The observation in this ^{31}P NMR work that Rh complexes with structures **2**, **3**, and **4** form readily with certain diphosphines and the observation that conclusions from IR, NMR, and reactor testing studies are consistent is support for our conclusion that complexes that confer high hydroformylation selectivity to linear aldehyde have three phosphine ligands coordinated to Rh at the instant that selectivity is determined. This can be accommodated without postulating a 20-electron intermediate (e.g., HRh(CO)(P∼P)(P∼P)[m](olefin) or HRh(CO)(P∼P)(PR_3)(olefin) by suggesting that a degree of CO ligand dissociation is possible under the conditions of temperature and CO partial pressure that prevail under hydroformylation conditions. Dissociation of the CO ligand rather than a phosphine ligand allows formation of

(7) Gordon, M. D.; Quin, L. D. *J. Magn. Reson* **1976**, *22*, 149.

18-electron intermediates (e.g., $HRh(P\sim P)(P\sim P)^m$(olefin) or $HRh(P\sim P)(PR_3)$(olefin)) that have three phosphine ligands coordinated to Rh at the step in the mechanism where Rh–H addition to coordinated olefin occurs (i.e., the selectivity determining step).

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Thallium-205 Nuclear Magnetic Resonance Study of Thallium(III) Halide Complexes in Aqueous Solutions

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Abstract: A combination of solution and solid-state ^{205}Tl NMR experiments is used to study the formation and geometry of TlX_n^{3-n} complexes (X = Cl, Br). The chemical shifts for the individual species and their stability constants are determined for dilute (0.05 M) and concentrated (1.0 and 2.6 M) aqueous Tl(III) solutions. The existence of $TlCl_5^{2-}$ and $TlCl_6^{3-}$ as well as at least one species higher than $TlBr_4^-$ in solution is shown. The species $TlCl_3$ is 300–400 ppm less shielded in aqueous solutions than in solid phase, indicating a structural difference. The chemical shifts obtained for the individual TlX_n^{3-n} complexes are compared with corresponding shifts for zinc(II) and cadmium(II) halide complexes.

The complexes formed in the thallium(III) halide system are among the strongest metal ion halide complexes known. Several investigations were made on this system,[2-20] and some interesting structural properties can be discerned. Thus, for example, there are indications[15,20] that in aqueous solutions of $Tl(ClO_4)_3$ only two water molecules are strongly bound to Tl^{3+} and that these are replaced by chloride when $TlCl(H_2O)_5^{2+}$ and $TlCl_2(H_2O)_4^+$ are formed. The stability constants and the enthalpy values[10-13,16,20] indicate some structural change between the second and third complex.

The existence of higher complexes $TlCl_n^{3-n}$ ($n > 4$) was for a long time a matter of controversy. In dilute solutions, where all of the emf, solubility, and calorimetric measurements were performed, the formation of higher complexes is generally claimed to be negligible: $K_5 = [TlX_5^{2-}]/([TlX_4^-][X^-]) < 0.07\ M^{-1}$ for X = Cl and $K_5 < 0.37\ M^{-1}$ for X = Br, at 25 °C.[10,11] (The exceptions are some emf works, where silver halide electrodes have been used.[3,4,8,9] These results are probably erroneous because of the oxidation of the electrodes by Tl(III), as was pointed out by some investigators.[10]) However, UV spectra of dilute Tl(III) solutions at very high chloride concentrations[19] indicate the formation of one higher species, $TlCl_5^{2-}$, with the stability constant $K_5 = 0.8\ (2)\ M^{-1}$.

Extraction data for dilute solutions are also interpreted in terms of weak bonding of the fifth chloride ligand ($K_5 = 0.3\ M^{-1}$),[5] although other workers using the same method found no evidence for complexes higher than $TlCl_4^-$ (at least not more than 3% of the total thallium concentration).[14]

In concentrated solutions, Raman spectra clearly show that, in the chloride system, at least one higher complex exists, probably $TlCl_6^{3-}$ ($K_{4,6} = [TlCl_6^{3-}]/([TlCl_4^-][Cl^-]^2) = 0.2\ M^{-2}$).[15,18] NMR data also indicate the formation of complexes with more than four chlorides per Tl(III).[6,7] Figgis[6] postulated that the most stable species at higher halide concentrations is $Tl_2X_9^{3-}$ (X = Cl, Br).

For determination of the compositions and structures of the complexes formed in aqueous solutions containing Tl(III) and one of the halides (Cl, Br), an X-ray diffraction study[21] was undertaken. For the interpretation of the diffraction data the distribution of Tl(III) among the different species has to be known for the concentrated solutions ($[Tl]_{tot} \geq 1$ M). However, all the available stability constants are determined for rather dilute solutions ($[Tl]_{tot} \leq 50$ mM). The aim of the present work is to estimate this distribution. In addition, the ^{205}Tl chemical shifts for the individual TlX_n^{3-n} complexes are obtained, and they may provide some structural information when compared with the chemical shifts for the corresponding solid-state coordination compounds with known structures. The shifts can also be compared with those determined for the halide complexes of the d^{10} ions Zn^{2+} and Cd^{2+}.

(1) (a) Department of Inorganic Chemistry. (b) Department of Physical Chemistry.
(2) Lee, A. G. "The Chemistry of Thallium"; Elsevier: Amsterdam, 1971; pp 44–91 and references cited therein.
(3) Benoit, R. *Bull. Soc. Chim. Fr.* **1949**, 518.
(4) Peschanski, D.; Valladas-Dubois, S. *Bull. Soc. Chim. Fr.* **1956**, 1170.
(5) Horrocks, D. L.; Voigt, A. F. *J. Am. Chem. Soc.* **1957**, *79*, 2440.
(6) Figgis, B. N. *Trans. Faraday Soc.* **1959**, *55*, 1075.
(7) Freeman, R.; Gasser, R. P. H.; Richards, R. E. *Mol. Phys.* **1959**, *2*, 301.
(8) Baysal, B. *Actes Congr. Int. Catal., 2nd* **1960**, *1*, 559 (*Chem. Abstr.* **1962**, *56*, 1140c).
(9) Busev, A. I.; Tiptsova, V. G.; Sokolova, T. A. *Vestnik Moskov. Univ. Khim.* **1960**, *II-6*, 42.
(10) Ahrland, S.; Grenthe, I.; Johansson, L.; Norén, B. *Acta Chem. Scand.* **1963**, *17*, 1567.
(11) Ahrland, S.; Johansson, L. *Acta Chem. Scand.* **1964**, *18*, 2125.
(12) Woods, M. J. M.; Gallagher, P. K.; Hugus, Z. Z.; King, E. L. *Inorg. Chem.* **1964**, *3*, 1313.
(13) Leden, I.; Ryhl, T. *Acta Chem. Scand.* **1964**, *18*, 1196.
(14) Nord., G.; Ulstrup, J. *Acta Chem. Scand.* **1964**, *18*, 307.
(15) Spiro, T. G. *Inorg. Chem.* **1965**, *4*, 731.
(16) Kul'ba, F. Y.; Mironov, V. E.; Mavrin, I. F. *Zh. Fiz. Khim.* **1965**, *39*, 2595.
(17) Yakovlev, Y. B.; Kul'ba, F. Y.; Mironov, V. E. *Zh. Neorg. Khim.* **1967**, *12*, 3283.
(18) Davies, E. D.; Long, D. A. *J. Chem. Soc. A* **1968**, 2050.
(19) Schmidt, K. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3549.
(20) Biedermann, G.; Spiro, T. G. *Chem. Scr.* **1971**, *1*, 155.
(21) Glaser, J.; Johansson, G. *Acta Chem. Scand., in press.*

0002-7863/81/1503-6642$01.25/0