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Synthesis and characterization of new titanium(II) carbonyls of stoichiometry $TiX_2(CO)_2(dmpe)_2$: an NMR study

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Abstract

The titanium(II) coordination complexes *trans*-$TiX_2(dmpe)_2$ (X = Cl, Br) react with carbon monoxide at low temperatures to afford thermally unstable eight-coordinate titanium(II) dicarbonyl complexes of stoichiometry $TiX_2(CO)_2(dmpe)_2$. The stoichiometries have been established from NMR studies; if ^{13}CO is employed, the NMR spectra correpond to the X and AB parts of AA'BB'XX' spin systems in the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra, respectively. Treatment of the mixed halide complex $TiClBr(dmpe)_2$ with CO gives the corresponding dicarbonyl complex $TiClBr(CO)_2(dmpe)_2$, which exhibits an ABCD spin system in its $^{31}P\{^1H\}$ NMR spectrum. The phosphorus–phosphorus, phosphorus–carbon, and carbon–carbon coupling constants for $TiCl_2(CO)_2(dmpe)_2$, $TiBr_2(CO)_2(dmpe)_2$, and $TiBrCl(CO)_2(dmpe)_2$ suggest that these complexes adopt bi-capped octahedral structures, with the halide ligands in the capping sites and the carbonyl ligands mutually *cis*. When cold (−78°C) solutions of $TiCl_2(dmpe)_2$ are exposed to carbon monoxide for short periods, an intermediate is detectable that slowly converts to $TiCl_2(CO)_2(dmpe)_2$. The intermediate contains one bidentate and one unidentate dmpe ligand as judged from its $^{31}P\{^1H\}$ NMR spectrum. There are two equal-intensity ^{13}C NMR resonances for the bound carbonyl groups at δ 453.6 and 456.7; these chemical shifts are quite unusual and are among the largest measured for any ^{13}C nucleus. Taken together, the data suggest that this intermediate is a 16-electron seven-coordinate complex of stoichiometry $TiCl_2(CO)_2(dmpe)(\eta^1\text{-}dmpe)$.

Keywords: Titanium; NMR; Phosphine complexes; Group 4; Carbonyl; Carbon-13

1. Introduction

The synthesis and characterization of Group 4 carbonyls remains a challenging and under-studied area of chemistry. For example, the first isolable binary carbonyls of the Group 4 elements, $[K(2.2.2\text{-crypt})]_2$-$[M(CO)_6]$ (M = Ti, Zr, and Hf) [1–3] have only recently been reported. Of the neutral binary carbonyls, the 18-electron heptacarbonyl $Ti(CO)_7$ has never been observed and the hexacarbonyl $Ti(CO)_6$ is only stable in a matrix below 30 K [4]. However, some Lewis-base-substituted derivatives of $Ti(CO)_7$ are significantly more stable. The first of these were reported by Wreford: $Ti(CO)_2(dmpe)_2(PF_3)$ [5] $Ti(CO)_3(dmpe)_2$ and $Ti(CO)_3(depe)_2$ [6] where dmpe and depe are the

bidentate phosphines 1,2-bis(dimethylphosphino)ethane and 1,2-bis(diethylphosphino)ethane, respectively. The structures of these complexes were described as either quadrilateral-face-capped trigonal prisms or capped octahedra. More recently, other seven-coordinate carbonyl complexes have been prepared [7–11], among these are the pentacarbonyl $[Ti(CO)_5(SnPh_3)_2^{2-}]$ [8] and the tetracarbonyls $Ti(CO)_4(trimpsi)$ [10] $Zr(CO)_4(trmpe)$ [7] and $Ti(CO)_4(Me_3tacn)$ [11] where trimpsi = tert-butyltris(dimethylphosphinomethyl) silane, trmpe = tris(dimethylphosphinomethyl)ethane, and Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane. The latter three complexes adopt 4:3 piano stool structures with the carbonyl and the phosphine (or amine) ligands occupying the fourfold and threefold faces, respectively. The bent-sandwich complex $(C_3H_3Bu^t_3)_2Hf(CO)$ [12] and the thermally unstable carbonyl $Zr(CO)(C_4H_6)_2(dmpe)$ [13] are also known.

The first Group 4 carbonyls to be described were

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the cyclopentadienyl derivatives $Cp_2M(CO)_2$ (M = Ti, Zr, Hf) and their substituted analogues [14,15]. However, there have been some notable recent additions to the class of cyclopentadienyl-stabilized Group 4 carbonyls. Salts of the zero valent anions $[CpM(CO)_4]^-$ and their pentamethylcyclopentadienyl analogues have been reported, and have been shown to adopt four-legged piano stool structures [8,16–18]. In addition, cyclopentadienyl complexes with bidentate phosphines such as $CpTi(CO)_2(dmpe)H$ [19,20], $CpZr(CO)_2$-$(dmpe)Cl$ [21], $Cp^*Hf(CO)_2(dmpe)Cl$ [22] have all been prepared, and all adopt pseudo-octahedral structures, if one considers the cyclopentadienyl group to occupy one coordination site.

Apart from the cyclopentadienyl species, there are few reports of the synthesis of carbonyl derivatives of Group 4 elements in the +2 oxidation state: Ellis has recently prepared species of stoichiometry $ZrX_2(CO)_2$-$(dmpe)_2$ and $HfX_2(CO)_2(dmpe)_2$, where X = Cl or I [23]. The X-ray crystal structure of the diiodohafnium derivative showed that this complex adopts a distorted square anti-prismatic structure in the solid state. The other derivatives were reported to be much less stable than the diiodohafnium complex and were only characterized by their infrared spectra in the ν(CO) region. Other eight-coordinate Group 4 complexes in the +2 oxidation state have also recently been prepared; species with the stoichiometry $[M(CO)_4(SnPh_3)_4^{2-}]$, where M is Zr or Hf [24].

In the course of exploring the reactivity of the titanium(II) complexes *trans*-$TiX_2(dmpe)_2$ (X = halide) [25], we have examined their behavior towards carbon monoxide; owing to the thermally sensitive nature of the products, we have studied these reactions by low temperature NMR spectroscopy. The results show that *trans*-$TiCl_2(dmpe)_2$ and *trans*-$TiBr_2(dmpe)_2$ react with carbon monoxide to afford the new titanium(II) carbonyl complexes $TiX_2(CO)_2(dmpe)_2$; these molecules are the first titanium analogues of the eight-coordinate zirconium and hafnium carbonyl complexes reported by Ellis. The first 16-electron carbonyl complex of a Group 4 element, $TiCl_2(CO)(dmpe)(\eta^1-dmpe)$, is also reported.

2. Results and discussion

When a solution of *trans*-$TiCl_2(dmpe)_2$ in toluene-d_8 is cooled to −72°C for 72 h under 3 atm. of CO, the initially brown–red solution changes color to light green and well-formed green crystals appear. Attempts to isolate the crystalline product have proven unsuccessful; if the CO pressure is released or if the solution is warmed above −70°C, the complex decomposes. Increasing the temperature of the solution causes the release of carbon monoxide from the metal center as

indicated by the formation of gas bubbles, and an associated color change from green to brown. If the solution is maintained below −40°C, this process is reversible. However, if solution is warmed to 25°C, no carbonyl species are formed upon recooling of the solution to −70°C. This result suggests that the metal center has been irreversibly oxidized. The reductive coupling of carbon monoxide to acetylene diolate groups by other low-valent early transition metal, actinide, and lanthanide complexes is known [26–40], related reductions of organic isonitriles to diaminoacetylene species have also been described [41–49]. In the present case, attempts to isolate the carbonaceous product formed upon reduction of CO by the metal center have thus far been unsuccessful.

If the reaction of $TiCl_2(dmpe)_2$ with CO is carried out in a sealed NMR tube, signals due to the green complex are readily seen. This complex has been formulated as the eight-coordinate titanium(II) dicarbonyl $TiCl_2(CO)_2(dmpe)_2$ (1) based on several lines of evidence. The $^{31}P\{^1H\}$ NMR spectrum of 1 consists of two triplets at δ 28.5 and δ 20.0 with an apparent J(PP) coupling constant of 26.8 Hz. Although this result clearly demonstrates that the product contains two dmpe ligands, the spin system described by the ^{31}P nuclei cannot be established from this spectrum alone since both an A_2B_2 and a deceptively simple AA'BB' spin system are consistent with the multiplet structure.

The number of carbonyl ligands bonded to the titanium center has been determined from experiments involving the reaction of *trans*-$TiCl_2(dmpe)_2$ with ^{13}CO. The $^{13}C\{^1H\}$ NMR spectrum of the ^{13}CO labelled complex contains a complex multiplet due to bound carbonyl groups at δ 272.4 (Fig. 1). The chemical shift of this resonance is much farther downfield than those of typical CO derivatives of the later transition ele-
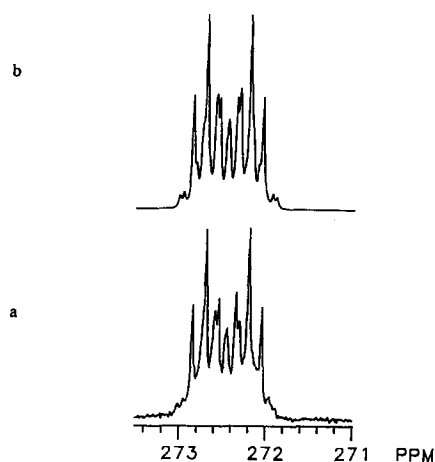

Fig. 1. 125 MHz $^{13}C\{^1H\}$ NMR spectrum of $TiCl_2(^{13}CO)_2(dmpe)_2$ (1), (a) observed at −70°C in toluene-d_8; (b) simulation, showing the X part of the AA'BB'XX' spin system where A = B = ^{31}P and X = ^{13}C.

ments, but is in fact consistent with the chemical shifts of other carbonyl complexes of the Group 4 elements (Table 1). The downfield ^{13}C NMR chemical shifts of such complexes have been discussed previously, and are evidently consequences of the unusually strong metal-to-ligand π-back-bonding in low-valent Group 4 carbonyls [10,20].

The ^{13}C{^{1}H} NMR spectrum demonstrates that the reaction of *trans*-TiCl$_2$(dmpe)$_2$ with CO yields a product in which there is only one carbonyl environment, and the number of CO ligands present in this product can be determined from an analysis of the ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra of the ^{13}CO isotopomer. Simulation of the ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra (Figs. 1 and 2) demonstrate conclusively that they correspond to the XX' and AA'BB' parts of an AA'BB'XX' spin system, respectively, where A, B = ^{31}P and X = ^{13}C. The chemical shifts and coupling constants used in the simulation are collected in Table 2. The ^{13}C{^{1}H} NMR pattern cannot be simulated successfully if it is assumed that the ^{31}P{^{1}H} NMR spin system is A$_2$B$_2$. These results establish that two carbon monoxide groups are bound to each titanium center.
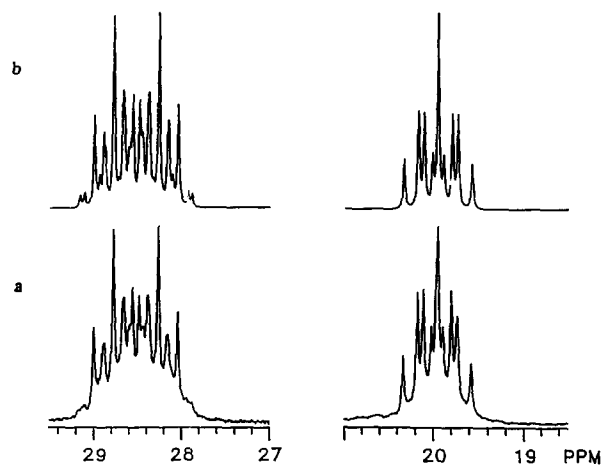

Fig. 2. 202 MHz ^{31}P{^{1}H} NMR spectrum of TiCl$_2$(^{13}CO)$_2$(dmpe)$_2$ (1) (a) observed at −70°C in toluene-d_8; (b) simulation, showing the AB part of the AA'BB'XX' spin system where A = B = ^{31}P and X = ^{13}C.

The ^{1}H and ^{13}C{^{1}H} NMR resonances due to the dmpe ligands show that there are four PCH$_3$ environments; this number is also consistent with the ^{31}P{^{1}H} NMR spectrum; i.e. there is a symmetry element pre-

Table 1
^{13}C NMR data for Group 4 carbonyl phosphine complexes [1]

Oxidation	Compound	^{13}C NMR	IR, ν_{CO} (cm^{-1})	Ref.
0	Ti(CO)$_5$(PMe$_3$)$_2$	259 (t, J(PC) = 8.4)		[8]
	Ti(CO)$_5$(dmpe)	266 (s, 4 CO)	1996, 1870	[8,9]
		239 (s, 1 CO)		
	[CpTi(CO)$_3$(PMe$_3$)$^-$]	299 (d, J(PC) = 20, 2 CO)	1823, 1712	[20]
		308 (d, J(PC) = 14, 1 CO)		
	[CpTi(CO)$_3$(PPh$_3$)$^-$]	300 (d, J(PC) = 14, 2 CO)	1831, 1721	[20]
		306 (d, J(PC) = 4, 1 CO)		
	[{CpTi(CO)$_3$}$_2$(μ-dmpe)$^{2-}$]	299 (t, J(PC) = 9, 2 CO)	1828, 1698	[20]
		308 (t, J(PC) = 6, 1 CO)		
	[CpTi(CO)$_2$(dmpe)$^-$]	320 (t, J(PC) = 18)	1658, 1563	[20]
	[Cp*Ti(CO)$_3$(PMe$_3$)$^-$]	304 (d, J(PC) = 17, 2 CO)	1815, 1704, 1676	[20]
		307 (d, J(PC) = 13, 1 CO)		
	[Cp*Ti(CO)$_2$(dmpe)$^-$]	316 (t, J(PC) = 17)	1680, 1600	[20]
	Ti(CO)$_4$(PMe$_3$)$_3$	275 (m)		[8]
	Ti(CO)$_4$['BuSi(CH$_2$PMe$_2$)$_3$]	277 (q, J(PC) = 8.2)	1915, 1820, 1780	[10]
	Ti(CO)$_4$[MeC(CH$_2$PMe$_2$)$_3$]	288 (q, J(PC) = 9)	1930, 1833, 1808	[7,9]
	Zr(CO)$_4$[MeC(CH$_2$PMe$_2$)$_3$]	284 (s)	1938, 1820	[7]
	Hf(CO)$_4$[MeC(CH$_2$PMe$_2$)$_3$]	282 (s)	1934, 1814	[7]
	Ti(CO)$_3$(dmpe)$_2$	301 (s), 282 (s), 268 (s)	1825, 1725	[6,9]
	Zr(CO)(C$_4$H$_6$)$_2$(dmpe)	248 (d, J(PC) = 12.5)		[13]
+2	TiCl$_2$(CO)$_2$(dmpe)$_2$	272 (m; see text)		this work
	TiCl$_2$(CO)$_2$(dmpe)(η^1-dmpe)	454 (d, J(PC) = 19), 457 (s)		this work
	TiBr$_2$(CO)$_2$(dmpe)$_2$	270 (m; see text)		this work
	HfI$_2$(CO)$_2$(dmpe)$_2$	288 (pentet, J(PC) = 11.2)	1890, 1783	[23]
	CpTi(CO)$_2$(dmpe)H	267 (t, J(PC) = 9)	1930, 1853	[19,20]
	Cp*Ti(CO)$_2$(dmpe)H	263 (t, J(PC) = 7)	1913, 1833	[20]
	CpZr(CO)$_2$(dmpe)Cl	250 (d, J(PC) = 16)	1955, 1885	[21]
	CpHf(CO)$_2$(dmpe)Cl	252 (d, J(PC) = 17)	1950, 1870	[21]
	Cp*Zr(CO)$_2$(dmpe)Cl	279 (s)	1923, 1810	[22]
	Cp*Hf(CO)$_2$(dmpe)Cl	283 (s)	1904, 1788	[22]
	Cp$_2$Ti(CO)(PMe$_3$)	299 (d, J(PC) = 3.9)	1864	[15]
	Cp$_2$Zr(CO)(PMe$_3$)	311 (d, J(PC) = 2.0)	1853	[15]
	Cp$_2$Hf(CO)(PMe$_3$)	273 (d, J(PC) = 2.0)	1842	[15]

[1] IR data included where available.

sent in the molecule that renders both dmpe ligands equivalent, but no symmetry element that relates the methyl groups within a dmpe ligand.

The bromo analogue, $TiBr_2(CO)_2(dmpe)_2$ (2) can be formed by repeating the reaction using *trans*-$TiBr_2(dmpe)_2$ in place of *trans*-$TiCl_2(dmpe)_2$. NMR spectroscopy shows that $TiBr_2(^{13}CO)_2(dmpe)_2$ possesses the same AA′BB′XX′ spin system as the chloro derivative. Simulations of the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra yield the parameters in Table 2; these parameters and the ^1H NMR chemical shifts and coupling constants are very similar to those of 1.

In order to determine the number of halide groups attached to the titanium center, *trans*-$TiCl_2(dmpe)_2$ and *trans*-$TiBr_2(dmpe)_2$ were mixed together in solution at ambient temperature in equimolar amounts to generate a mixture of *trans*-$TiCl_2(dmpe)_2$, *trans*-$TiBr_2$-$(dmpe)_2$, and the mixed halide complex $TiBrCl(dmpe)_2$ (the latter compound is new and its ^1H NMR parameters are given in Section 3). A solution of this mixture was then cooled to $-72°C$ and pressurized to 30 psi with carbon monoxide. The number of halide groups attached to the titanium center can then be determined by counting the number of different carbonyl species formed: (1) if only one species is present, the complexes must be dications, $[Ti(CO)_2(dmpe)_2^{2+}]$, and both of the halide groups must be counter ions, (2) if two species are present, the complexes must be mono-cations, $[TiX(CO)_2(dmpe)_2^+]$, or (3) if three species are present, the complexes must be electrically neutral, $TiX_2(CO)_2(dmpe)_2$, and both halide groups must be bound to titanium.
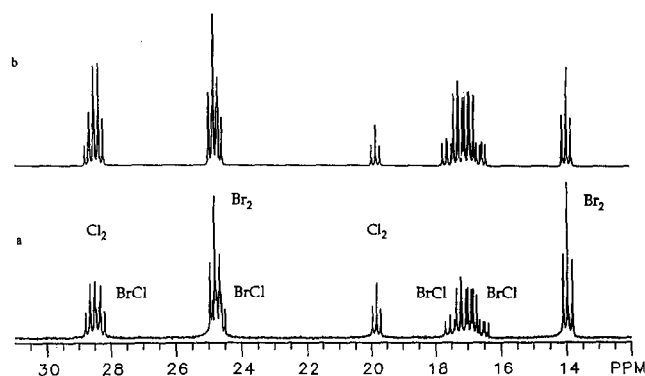

Fig. 3. 202 MHz $^{31}P\{^1H\}$ NMR spectrum of a mixture of $TiCl_2(CO)_2(dmpe)_2$ (1), $TiBr_2(CO)_2(dmpe)_2$ (2) and TiClBr-$(CO)_2(dmpe)_2$ (3), (a) observed at $-70°C$ in toluene-d_8; (b) simulated spectrum.

The $^{31}P\{^1H\}$ spectrum obtained (Fig. 3) shows the presence of three species. There are two resonances due to $TiCl_2(CO)_2(dmpe)_2$, two resonances due to $TiBr_2(CO)_2(dmpe)_2$, and four additional resonances due to the mixed halide species $TiBrCl(CO)_2(dmpe)_2$ (3). These results unambiguously establish the identities of all of these carbonyl compounds as eight-coordinate 18-electron species of stoichiometry $TiX_2(CO)_2$-$(dmpe)_2$. The presence of four ^{31}P environments for $TiClBr(CO)_2(dmpe)_2$ shows that this complex possesses no symmetry. This further confirms that the triplets observed in the $^{31}P\{^1H\}$ spectrum of $TiCl_2$-$(CO)_2(dmpe)_2$ are in fact AA′BB′ patterns that are deceptively simple due to the presence of a large $J(PP)$

Table 2
$^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data for the new titanium(II) carbonyl complexes [1]

Compound	Spin system	δ_P	$J(PP)$	$J(PC)$	δ_C, $J(CC)$
$TiCl_2(^{13}CO)_2(dmpe)_2$	AA′BB′XX′	$\delta_A = 28.5$	$J_{AA'} = 30.4$	$J_{AX} = 60.5$	$\delta_X = 272.4$
		$\delta_B = 20.0$	$J_{AB} = 26.8$	$J_{AX'} = 2.5$	$J_{XX'} = 3.9$
			$J_{AB'} = 26.8$	$J_{BX} = 19.1$	
			$J_{BB'} = 71.5$	$J_{BX'} = 19.1$	
$TiBr_2(^{13}CO)_2(dmpe)_2$	AA′BB′XX′	$\delta_A = 24.8$	$J_{AA'} = 30.0$	$J_{AX} = 60.5$	$\delta_X = 269.6$
		$\delta_B = 14.0$	$J_{AB} = 27.7$	$J_{AX'} = 2.5$	$J_{XX'} = 4.0$
			$J_{AB'} = 27.7$	$J_{BX} = 19.0$	
			$J_{BB'} = 71.5$	$J_{BX'} = 19.0$	
$TiBrCl(CO)_2(dmpe)_2$	ABCD	$\delta_A = 28.7$	$J_{AB} = 27.4$		
		$\delta_B = 24.8$	$J_{AC} = 26.7$		
		$\delta_C = 17.4$	$J_{AD} = 32.0$		
		$\delta_D = 16.8$	$J_{BC} = 30.9$		
			$J_{BD} = 21.0$		
			$J_{CD} = 71.5$		
$TiCl_2(^{13}CO)_2(dmpe)(\eta^1$-dmpe)	ABCDXY	$\delta_A = 25.2$	$J_{AB} = 27$	$J_{BX} = 19$	$\delta_X = 453.6$
		$\delta_B = 20.7$	$J_{AC} = 54$		$\delta_Y = 456.7$
		$\delta_C = 6.8$			
		$\delta_D = -46.9$			

[1] Chemical shifts are reported in ppm and coupling constants are reported in Hz. Coupling constants that are not specified are zero.

coupling of 71.5 Hz. The remaining $^{31}P\{^1H\}$ NMR parameters for $TiBrCl(CO)_2(dmpe)_2$ are collected in Table 2.

In theory, it should be possible to establish the arrangement of the ligands in the $TiX_2(CO)_2(dmpe)_2$ complexes from the $J(PP)$, $J(PC)$ and $J(CC)$ coupling constants. The data in Table 2 show that there is one large (71.5 Hz) $J(PP)$ coupling constant in the $TiX_2(CO)_2(dmpe)_2$ complexes; the remaining $J(PP)$ coupling are much smaller (ca. 30 Hz). The 71.5 Hz coupling suggests that two of the phosphorus nuclei are trans to each other (or nearly so). The chemical shifts of the two strongly coupled ^{31}P nuclei in the mixed halide complex appear at chemical shifts of δ 17.4 and δ 16.8 that are intermediate between those of δ 20.0 for the dichloro complex and δ 14.0 for the dibromo complex. The small 0.6 ppm difference between the chemical shifts of the strongly coupled ^{31}P nuclei in $TiBrCl(CO)_2(dmpe)_2$ is consistent with the view that these phosphorus nuclei are trans to each other; if they had been trans to halide, a larger difference in their chemical shifts would have been seen.

The probable locations of the two phosphorus nuclei that are not trans to each other can be established from the $J(PC)$ coupling constants to the labelled carbonyl groups. Notably, these phosphines are involved in one large $J(PC)$ coupling of 60.5 Hz and one smaller coupling of 2.5 Hz. The magnitudes of the couplings suggest that each of these phosphorus nuclei is approximately trans to one carbonyl group and cis to the other.

Finally, the relative locations of the carbonyl groups in the coordination sphere can be established from the $J(CC)$ coupling constant. In $TiCl_2(CO)_2(dmpe)_2$, this coupling is small ($J(CC) = 3$ Hz), which suggests that the carbonyl ligands are mutually cis [50–53].

Of the other $J(PP)$ and $J(PC)$ coupling constants in Table 2, some of those involving the two mutually trans phosphorus nuclei are only approximate; due to the large value of the $J_{BB'}$ coupling (71.5 Hz) and the observed line widths of the NMR peaks (7 Hz), the appearance of the spectrum is unchanged even if J_{AB} and $J_{AB'}$ differ by as much as 12 Hz, provided that the sum of J_{AB} and $J_{AB'}$ remains constant. A similar situation pertains for the J_{BX} and $J_{JB'}$ coupling constants. The uncertainties in these coupling constants do not, however, affect conclusions about the possible arrangement of ligands in the $TiX_2(CO)_2(dmpe)_2$ complexes. The mixed halide complex $TiBrCl(CO)_2(dmpe)_2$ (3) is free of the second order effects present in 1 and 2; simulation of its $^{31}P\{^1H\}$ NMR spectrum shows that the coupling constants corresponding to J_{AB} and $J_{AB'}$ in 1 and 2 are not equal, but differ by 12 Hz.

The NMR parameters for $TiCl_2(CO)_2(dmpe)_2$, $TiBr_2(CO)_2(dmpe)_2$, and $TiBrCl(CO)_2(dmpe)_2$ are most consistent with bi-capped octahedral structures, with the halide ligands in the capping sites and the carbonyl ligands mutually cis:
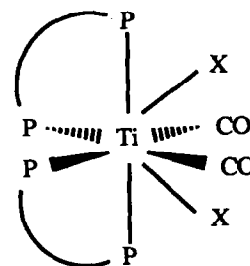
In particular, this arrangement places two of the phosphorus nuclei in mutually trans positions, two of the phosphorus nuclei approximately trans to carbonyl groups, and the carbonyl groups mutually cis. If one assumes that the $TiX_2(CO)_2(dmpe)_2$ complexes adopt structures based upon a trigonal dodecahedron or a square anti-prism, the NMR data are much more difficult to rationalize.

A point of concern, however, is the lack of precedence for a phosphine-to-carbonyl coupling constant as large as 60 Hz. Trans $J(PC)$ coupling constants between phosphines and carbonyl groups of up to 40 Hz have been seen in other transition metal complexes [50–53]. Table 1 contains a list of reported Group 4 carbonyl phosphine complexes in various oxidation states. Of those complexes for which $J(PC)$ values are reported, the largest such coupling is only 20 Hz. Another point of concern is that the resonances assigned to the phosphorus nuclei trans to carbonyl are downfield of those due to the phosphorus nuclei trans to each other. The reverse situation is usually observed owing to the high trans-influence ability of carbonyl ligands [54]. The unusual coupling constants and chemical shifts probably reflect the atypical electronic nature of the low-valent titanium(II) center, which has unusually high energy d-orbitals as a consequence of the low effective nuclear charge and the low oxidation state [10]. Changes in the relative importance of σ and π bonding and in the paramagnetic shielding contribution to the chemical shift (compared with other transition metal complexes) could account for the unexpectedly large $J(PC)$ coupling constants and the relative chemical shifts of the chemically inequivalent ^{31}P nuclei.

The structures proposed for the $TiX_2(CO)_2(dmpe)_2$ complexes differ from the distorted square-anti-prismatic structure of $HfI_2(CO)_2(dmpe)_2$ established crystallographically [23]. At first glance, there are some similarities between the ^{13}C and $^{31}P\{^1H\}$ NMR spectra of $HfI_2(CO)_2(dmpe)_2$ and those of the $TiX_2(CO)_2$-$(dmpe)_2$ complexes; for example, two phosphorus environments and one carbonyl environment were observed for $HfI_2(CO)_2(dmpe)_2$. Although the number of environments observed for the hafnium complex is consistent with a square anti-prismatic structure, the pattern observed for the carbonyl resonance is unex-

pected. Specifically, the carbonyl resonance was reported to be a binomial pentet, i.e. a first order NMR pattern. In order to yield the observed ^{13}C NMR pentet, the chemically inequivalent phosphorus atoms must either be accidentally coupled with identical coupling constants to the carbonyl ligand, or must be engaged in a dynamic process that averages some of the coupling constants but does not exchange the chemically inequivalent phosphorus sites. In any case, the shape of the carbonyl resonance of $HfI_2(CO)_2$-$(dmpe)_2$ differs significantly from the second order patterns seen for the $TiX_2(CO)_2(dmpe)_2$ complexes, and thus it is reasonable to conclude that the latter may very well adopt structures in solution different from that observed for the former in the solid state.

2.1. Intermediates in the carbonylation of $TiCl_2(dmpe)_2$

When cold ($-78°C$) solutions of $TiCl_2(dmpe)_2$ are exposed to carbon monoxide for short periods, an intermediate is detectable that slowly converts to $TiCl_2(CO)_2(dmpe)_2$. The intermediate is characterized by the presence of four ^{31}P{^{1}H} NMR resonances (δ 25.2, 20.7, 6.8, and -46.8) (Fig. 4) and two equal-intensity ^{13}C{^{1}H} NMR resonances for bound carbonyl groups (δ 453.6 and 456.7) (Fig. 5). The ^{31}P{^{1}H} NMR resonance at δ -46.8 is close to that of free dmpe, and indicates the presence of a unidentate dmpe ligand. Taken together, the data suggest that this intermediate is a seven-coordinate complex of stoichiometry $TiCl_2$-$(CO)_2(dmpe)(\eta^1$-dmpe) (4). The $^2J(PP)$ and $^2J(PC)$ coupling constants in 4 are within the normal range (Table 2), and are consistent with a variety of seven-coordinate geometries. The ^{31}P{^{1}H} NMR resonance at δ -46.8 is broad in comparison to the other ^{31}P{^{1}H} NMR resonances, which suggests that this nucleus is involved in an exchange process.

The ^{13}C{^{1}H} NMR chemical shifts of the carbonyl resonances of 4 are unusual and are among the largest measured for any ^{13}C nucleus. The only previously
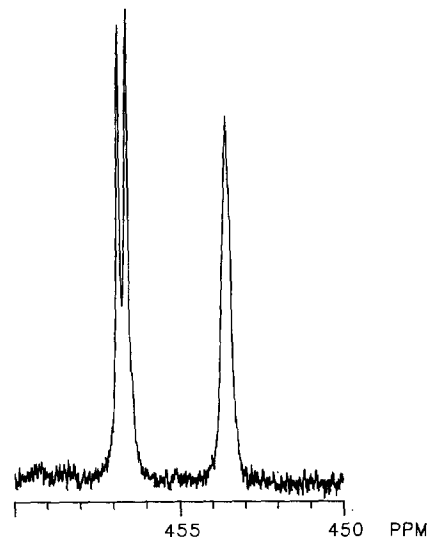
Fig. 5. 75 MHz ^{13}C{^{1}H} NMR spectrum of $TiCl_2(CO)_2(dmpe)(\eta^1$-dmpe) (4) at $-80°C$ in toluene-d_8.

reported resonances in this region are exhibited by certain metal carbides and carbocations [55–58]; such functional groups are unlikely to be present in 4 as judged by the high solubility of this complex in toluene at $-80°C$. Furthermore, it is apparent that the two carbonyl ligands have not undergone a reductive coupling to a coordinated acetylene diolate ligand, since the $J(CC)$ coupling constant is so small as to be unresolvable. The downfield chemical shift of the carbonyl resonance in 4 may be due to the contribution of the paramagnetic term σ_{para} to the chemical shift: even for diamagnetic compounds there can be a substantial effect of low-lying paramagnetic excited states on chemical shifts [54]. Such effects are responsible, inter alia, for the upfield chemical shifts in transition metal hydrides. The presence of low-lying paramagnetic states for 4 is also suggested by the fact that its ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR resonances at $-70°C$ are about six times broader than those of the eight-coordinate complex 1 (the line widths of the latter are ca. 1.5 Hz and ca. 7 Hz in the ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra, respectively). The current complex is the first 16-electron early transition metal carbonyl for which ^{13}C NMR data has been obtained. It is possible that these downfield ^{13}C NMR chemical shifts will prove to be characteristic of such species.

The structure of 4 suggests that $TiCl_2(dmpe)_2$ reacts with CO in the following manner: one of the arms of one dmpe ligand dissociates to yield the five-coordinate species $TiCl_2(dmpe)(\eta^1$-dmpe), two molecules of CO coordinate to form seven-coordinate $TiCl_2(CO)_2$-$(dmpe)(\eta^1$-dmpe), and then the unidentate dmpe ligand slowly re-chelates to form the ultimate product, the eight-coordinate species $TiCl_2(CO)_2(dmpe)_2$. The first step in this sequence, dissociation of one arm of a

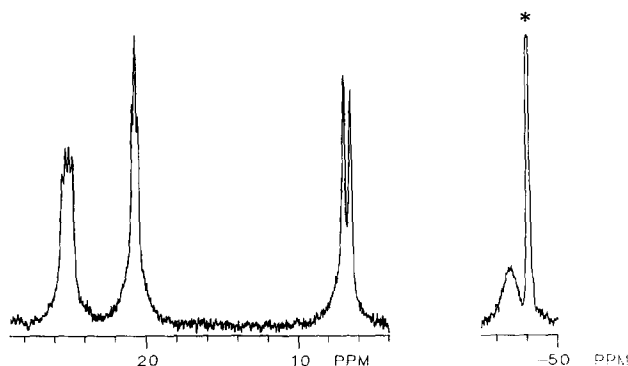Fig. 4. 121 MHz ^{31}P{^{1}H} NMR spectrum of $TiCl_2(CO)_2(dmpe)(\eta^1$-dmpe) (4) at $-80°C$ in toluene-d_8.

dmpe ligand to form a five-coordinate intermediate, is also seen in the reactions of $TiCl_2(dmpe)_2$ with other Lewis bases such as alkenes, nitriles and isonitriles [59].

3. Experimental section

All operations were carried out in vacuum or under argon. The titanium(II) coordination complexes trans-$TiCl_2(dmpe)_2$ [25] and trans-$TiBr_2(dmpe)_2$ [60] were prepared as reported elsewhere. Carbon monoxide (Matheson) and ^{13}CO (Isotec) were used as received. The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR data were obtained on a General Electric GN-500 spectrometer at frequencies of 500 MHz, 125 MHz, and 202 MHz, respectively, and on a General Electric GN-300NB instrument at frequencies of 300 MHz, 75 MHz and 121 MHz, respectively. The NMR chemical shifts are reported in δ units (positive shifts to higher energies) relative to $SiMe_4$ (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Toluene-d_8 was distilled from sodium under argon and was degassed by three freeze-pump-thaw cycles before use. Attempts to measure the IR spectra of the titanium carbonyl compounds reported herein were unsuccessful due to the limitations of our apparatus; our solution IR cell did not permit us to obtain spectra at low temperatures and at elevated CO pressures.

3.1. Dichlorodicarbonylbis[1,2-bis(dimethylphosphino)ethane]titanium(II), $TiCl_2(CO)_2(dmpe)_2$

A sample of trans-$TiCl_2(dmpe)_2$ (20.0 mg, 0.048 mmol) was dissolved in toluene-d_8 (1 ml), and a portion of this solution (0.75 ml) was transferred into an NMR tube fitted with a gas adapter. The NMR tube was cooled to −72°C and pressurized to 30 psi with carbon monoxide. The NMR tube was then frozen at −196°C and flame-sealed. The tube was stored at −72°C for 48 h before examination by NMR spectroscopy. The ^{13}CO labelled analogue was prepared similarly. ^{1}H NMR (toluene-d_8, −70°C): δ 0.75 (d, $J(PH) = 6$ Hz, PMe$_2$); 1.38 (d, $J(PH) = 10$ Hz, PMe$_2$); 1.62 (t, $J(PH) = 4.5$ Hz, PMe$_2$); 1.22 (br m, PCH$_2$); 1.85 (t, $J(PH) = 14$ Hz, PCH$_2$). $^{13}C\{^{1}H\}$ NMR (toluene-d_8, −70°C): δ 10.3 (d, $J(PC) = 13$ Hz, PMe$_2$); 10.6 (d, $J(CP) = 23$ Hz, PMe$_2$); 11.4 (t, $J(PC) = 10$ Hz, PMe$_2$); 12.6 (t, $J(PC) = 7.5$ Hz, PMe$_2$); 23.6 (br s, PCH$_2$); 30.5 (br s, PCH$_2$). ^{13}C NMR data for the carbonyl resonance are given in Table 2.

3.2. Dibromodicarbonylbis[1,2-bis(dimethylphosphino)ethane]titanium(II), $TiBr_2(CO)_2(dmpe)_2$

A sample of trans-$TiBr_2(dmpe)_2$ (20.0 mg, 0.039 mmol) was dissolved in toluene-d_8 (1 ml), and a portion of this solution (0.75 ml) was transferred into a NMR tube fitted with a gas adapter. The NMR tube was cooled to −72°C, pressurized to 30 psi with carbon monoxide, frozen at −196°C, and flame-sealed. The tube was then stored at −72°C for 48 h before examination by NMR spectroscopy. The ^{13}CO labelled analogue was prepared similarly. ^{1}H NMR (toluene-d_8, −80°C): δ 0.80 (d, $J(PH) = 6$ Hz, PMe$_2$); 1.48 (d, $J(PH) = 10$ Hz, PMe$_2$), 1.59 (t, $J(PH) = 2.5$ Hz, PMe$_2$); 1.83 (t, $J(PH) = 4$ Hz, PMe$_2$).

3.3. Chlorobromobis[1,2-bis(dimethylphosphino)ethane]titanium(II), $TiClBr(dmpe)_2$

A mixture of trans-$TiBr_2(dmpe)_2$ (7.0 mg, 0.0138 mmol) and trans-$TiCl_2(dmpe)_2$ (5.0 mg, 0.0138 mmol) was dissolved in toluene-d_8 (1.00 ml), and a portion of the resulting solution (0.75 ml) was transferred into an NMR tube. This solution contained a 3:3:2 mixture of trans-$TiCl_2(dmpe)_2$, trans-$TiBr_2(dmpe)_2$, and the mixed halide complex $TiClBr(dmpe)_2$. The ^{1}H NMR spectrum of the latter complex in toluene-d_8 at 25°C shows that it is paramagnetic like its dichloro and dibromo analogues: δ −4.70 (s, fwhm = 100 Hz, PMe$_2$) and δ 10.40 (s, fwhm = 125 Hz, PCH$_2$).

3.4. Chlorobromodicarbonylbis[1,2-bis(dimethylphosphino)ethane]titanium(II), $TiClBr(CO)_2(dmpe)_2$

A mixture of trans-$TiBr_2(dmpe)_2$ (7.0 mg, 0.0138 mmol) and trans-$TiCl_2(dmpe)_2$ (5.0 mg, 0.0138 mmol) was dissolved in toluene-d_8 (1.00 ml), and a portion of the resulting solution (0.75 ml) was transferred into an NMR tube fitted with a gas adapter. The NMR tube was cooled to −72°C, pressurized to 30 psi with carbon monoxide, frozen at −196°C, and flame sealed. The tube was then stored at −72°C for 48 h before examination by NMR spectroscopy. The solution contained a 1:2:1 mixture of $TiCl_2(CO)_2(dmpe)_2$, $TiClBr(CO)_2(dmpe)_2$ and $TiBr_2(CO)_2(dmpe)_2$.

References

[1] K.M. Chi, S.R. Frerichs, S.B. Philson and J.E. Ellis, Angew. Chem., Int. Ed. Engl., 27 (1987) 1190.
[2] K.M. Chi, S.R. Frerichs, S.B. Philson and J.E. Ellis, J. Am. Chem. Soc., 110 (1988) 303.

[3] K.M. Chi and J.E. Ellis, *J. Am. Chem. Soc.*, *112* (1990) 6022.

[4] R. Busby, W. Klotzbucher and G.A. Ozin, *Inorg. Chem.*, *16* (1977) 822.

[5] S.S. Wreford, M.B. Fischer, J.-S. Lee, E.J. James and S.C. Nyburg, *J. Chem. Soc., Chem. Commun.*, (1981) 458.

[6] P.J. Domaille, R.L. Harlow and S.S. Wreford, *Organometallics*, *1* (1982) 935.

[7] D.W. Blackburn, K.M. Chi, S.R. Frerichs, M.L. Tinkham and J.E. Ellis, *Angew. Chem., Int. Ed. Engl.*, *27* (1988) 437.

[8] K.M. Chi, S.R. Frerichs and J.E. Ellis, *J. Chem. Soc., Chem. Commun.*, (1988) 1013.

[9] K.M. Chi, S.R. Frerichs, B.K. Stein, D.W. Blackburn and J.E. Ellis, *J. Am. Chem. Soc.*, *110* (1988) 163.

[10] T.G. Gardner and G.S. Girolami, *Organometallics*, *6* (1987) 2551.

[11] J.E. Ellis, A.J. DiMaio, A.L. Rheingold and B.S. Haggerty, *J. Am. Chem. Soc.*, *114* (1992) 10676.

[12] F.G.N. Cloke, M.F. Lappert, G.A. Lawless and A.C. Swain, *J. Chem. Soc., Chem. Commun.*, (1987) 1667.

[13] R.P. Beatty, S. Datta and S.S. Wreford, *Inorg. Chem.*, *18* (1979) 3139.

[14] D.J. Sikora, D.W. Macomber and M.D. Rausch, *Adv. Organomet. Chem.*, *25* (1986) 317.

[15] L.B. Kool, M.D. Rausch, H.G. Alt, M. Herberhold, B. Wolf and H. Thewalt, *J. Organomet. Chem.*, *297* (1985) 159.

[16] B.A. Kelsey and J.E. Ellis, *J. Am. Chem. Soc.*, *108* (1986) 1344.

[17] S.R. Frerichs and J.E. Ellis, *J. Organomet. Chem.*, *359* (1989) C41.

[18] B.A. Kelsey and J.E. Ellis, *J. Chem. Soc., Chem. Commun*, (1986) 331.

[19] S.R. Frerichs, B.K. Stein and J.E. Ellis, *J. Am. Chem. Soc.*, *109* (1987) 5558.

[20] J.E. Ellis, B.K. Stein and S.R. Frerichs, *J. Am. Chem. Soc.*, *115* (1993) 4066.

[21] Y. Wielstra, S. Gambarotta, J.B. Roedelof and M.Y. Chiang, *Organometallics*, *7* (1988) 2177.

[22] B.K. Stein, S.R. Frerichs and J.E. Ellis, *Organometallics*, *6* (1987) 2017.

[23] J.E. Ellis, S.R. Frerichs and K.M. Chi, *Organometallics*, *9* (1990) 2858.

[24] J.E. Ellis, K.M. Chi, A.J. DiMaio, S.R. Frerichs, J.R. Stenzel, A.L. Rheingold and B.S. Haggerty, *Angew. Chem., Int. Ed. Engl.*, *30* (1991) 194.

[25] G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1985) 1339.

[26] J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, *J. Am. Chem. Soc.*, *100* (1978) 2716.

[27] P.T. Wolczanski and J.E. Bercaw, *Acc. Chem. Res.*, *13* (1980) 121.

[28] P.J. Fagan, K.G. Moloy and T.J. Marks, *J. Am. Chem. Soc.*, *103* (1981) 6959.

[29] D.H. Berry, J.E. Bercaw, A.J. Jircitano and K.B. Mertes, *J. Am. Chem. Soc.*, *104* (1982) 4712.

[30] D.A. Katahira, K.G. Moloy and T.J. Marks, *Organometallics*, *1* (1982) 1723.

[31] S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc.*, *105* (1983) 7295.

[32] W.J. Evans, A.L. Wayda, W.E. Hunter and J.L. Atwood, *J. Chem. Soc., Chem. Commun.*, (1981) 706.

[33] W.J. Evans, J.W. Grate, L.A. Hughes, H. Zhang and J.L. Atwood, *J. Am. Chem. Soc.*, *107* (1985) 3728.

[34] R.P. Planalp and R.A. Andersen, *J. Am. Chem. Soc.*, *105* (1983) 7774.

[35] G. Erker, P. Czisch, R. Schlund, K. Angermund and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, *25* (1986) 364.

[36] J. Arnold and T.D. Tilley, *J. Am. Chem. Soc.*, *107* (1985) 6409.

[37] R.N. Vrtis, C.P. Rao, S.G. Bott and S.J. Lippard, *J. Am. Chem. Soc.*, *110* (1988) 7564.

[38] J.D. Protasiewicz and S.J. Lippard, *J. Am. Chem. Soc.*, *113* (1991) 6564.

[39] R. Toreki, R.E. LaPointe and P.T. Wolczanski, *J. Am. Chem. Soc.*, *109* (1987) 7558.

[40] P.A. Bianconi, I.D. Williams, M.P. Engeler and S.J. Lippard, *J. Am. Chem. Soc.*, *108* (1986) 311.

[41] C.T. Lam, P.W.R. Corfield and S.J. Lippard, *J. Am. Chem. Soc.*, *99* (1977) 617.

[42] P.W.R. Corfield, L.M. Baltusis and S.J. Lippard, *Inorg. Chem.*, *20* (1981) 922.

[43] J.C. Dewan, C.M. Giandomenico and S.J. Lippard, *Inorg. Chem.*, *20* (1981) 4069.

[44] C.M. Giandomenico, C.T. Lam and S.J. Lippard, *J. Am. Chem. Soc.*, *104* (1982) 1263.

[45] C. Caravana, C.M. Giandomenico and S.J. Lippard, *Inorg. Chem.*, *21* (1982) 1860.

[46] R. Hoffmann, C.N. Wilker, S.J. Lippard, J.L. Templeton and D.J. Brower, *J. Am. Chem. Soc.*, *105* (1983) 146.

[47] F.A. Cotton and W.J. Roth, *J. Am. Chem. Soc.*, *105* (1983) 3734.

[48] F.A. Cotton, S.A. Duraj and W.J. Roth, *J. Am. Chem. Soc.*, *106* (1984) 6987.

[49] D. Lenz, I. Brüddgam and H. Hartl, *Angew. Chem., Int. Ed. Engl.*, *23* (1984) 525.

[50] A.R. Hermes and G.S. Girolami, *Organometallics*, *7* (1988) 394.

[51] S. Aime and D. Osella, *J. Chem. Soc., Chem. Commun.*, (1981) 300.

[52] G. Cardaic, G. Reichback and G. Bellachioma, *Inorg. Chem.*, *23* (1984) 2936.

[53] M. Tachikawa, S.E. Richter and J.R. Shapley, *J. Organomet. Chem.*, *128* (1977) C9.

[54] P.S. Pregosin and R.W. Kunz, in P. Diehl, E. Fluck and R. Kosfeld (eds.), ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes, Springer, New York, 1979.

[55] J.A. Hriljac, S. Harris and D.F. Shriver, *Inorg. Chem.*, *27* (1988) 816.

[56] J.A. Hriljac, E.M. Holt and D.F. Shriver, *Inorg. Chem.*, *26* (1987) 2943.

[57] G.B. Karet, R.L. Espe, C.L. Stern and D.F. Shriver, *Inorg. Chem.*, *31* (1992) 2658.

[58] M.H. Chisholm, K. Folting and J.C. Huffman, *J. Am. Chem. Soc.*, *107* (1985) 3722.

[59] M.D. Spencer, S.R. Wilson and G.S. Girolami, unpublished.

[60] J.A. Jensen, PhD. Thesis, University of Illinois, 1988.