1893.9 cm^{-1}).[42] The small value of θ in the former case (**3b**) is what would be expected for a *pyramidal* geometry, with perhaps CH_4 filling the "vacant site", while the larger value in the second case (**3a**) indicates a planar geometry (Scheme II). The reactivities of the coordinatively unsaturated species were demonstrated by their recombination with ejected CO and with other reactants doped into the matrices, e.g. $V(\eta^5\text{-}C_5H_5)(CO)_3(N_2)$ and $V(\eta^5\text{-}C_5H_5)(CO)_{4-n}(C_2H_4)_n$ (n = 1, 2). Calculations of the OC–V–CO angle (110°) and the interaction force constant (62.9 N m^{-1}) and comparison with related data (k_{12} = 32.2 and k_{13} = 46.9 N m^{-1}) for $V(\eta^5\text{-}C_5H_5)(CO)_4$ suggest that the bis(ethylene) species exists as the trans isomer, i.e. *trans*-$V(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)_2$. Although kinetic studies[14] and quantum yield measurements[4] favored dissociative paths for the thermal and photochemical substitution reactions of $V(\eta^5\text{-}C_5H_5)(CO)_4$, an associative pathway could not be ruled out. The possibility that a C_5H_5 could change its hapticity, e.g. $\eta^5 \rightleftharpoons \eta^3$ (ring slippage or partial dechelation), provides a feasible pathway for associative mechanisms in metal–cyclopentadienyl complexes. Such a hapticity change has been suggested for $Co(\eta^5\text{-}C_5H_5)(CO)_2$ in a CO matrix.[31] It is proposed, therefore, that the species formed on long wavelength photolysis of $V(\eta^5\text{-}C_5H_5)(CO)_4$ in all matrices (Ar, CH_4, N_2, CO) is the $\eta^3\text{-}C_5H_5$ species $V(\eta^3\text{-}C_5H_5)(CO)_4$ and that in a CO matrix this species may add a further CO ligand to give $V(\eta^3\text{-}C_5H_5)(CO)_5$ (18-electron species) or $V(\eta^1\text{-}C_5H_5)(CO)_5$ (16-electron species) depending on the electronic requirements for a filled shell versus steric crowding. The evidence in favor of ring-slippage $\eta^3\text{-}C_5H_5$ species suggests that the possible contribution of S_N2 pathways in solution thermal and photochemical reactions should be reevaluated for $V(\eta^5\text{-}C_5H_5)(CO)_4$.

Acknowledgment. We thank the Universiti Teknologi Malaysia for support (to R.B.H.) and the SERC for a grant (to A.J.R.).

Registry No. $V(\eta^5\text{-}C_5H_5)(CO)_4$, 12108-04-2; $V(\eta^3\text{-}C_5H_5)(CO)_4$, 120610-57-3; $V(\eta^5k\text{-}C_5H_5)(CO)_3$, 120610-58-4; $V(\eta^5\text{-}C_5H_5)(CO)_2$, 120610-59-5; $V(\eta^5\text{-}C_5H_5)(CO)$, 120610-60-8; $V(\eta^5\text{-}C_5H_5)(CO)_3(N_2)$, 120610-61-9; $V(\eta^5\text{-}C_5H_5)(CO)_3(C_2H_4)$, 120610-62-0; $V(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)_2$, 120610-63-1; $V(\eta\text{-}C_5H_5)(CO)_5$, 120636-93-3; $V(\eta^5\text{-}C_5H_5)(^{12}CO)_3(^{13}CO)$, 99629-80-8; $V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)_2$ (isomer 1), 120610-64-2; $V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)_2$ (isomer 2), 120707-79-1; $V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)_3$, 120610-65-3; $V(\eta^5\text{-}C_5H_5)(^{13}CO)_4$, 120610-66-4; $V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)$, 120610-67-5; $V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)_2$, 120610-68-6; $V(\eta^5\text{-}C_5H_5)(^{13}CO)_3$, 120610-69-7; $V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)$, 120610-70-0; $V(\eta^5\text{-}C_5H_5)(^{13}CO)_2$, 120610-71-1; $V(\eta^5\text{-}C_5H_5)(^{13}CO)$, 120610-72-2.

(Methylenephosphoranyl)methyl, Phosphinylmethyl, and Phosphinothioylmethyl Complexes of Tantalum

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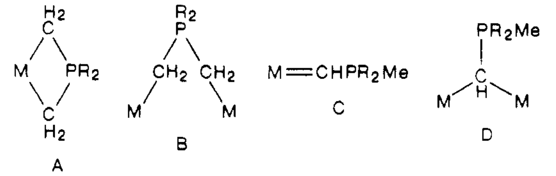
Received July 25, 1988

The reactions of lithium salts of the anionic ylides $(CH_2)_2PRR'$ (R = R′ = Me; R = Me, R′ = Ph; R = R′ = Ph) and pseudoylides $(CH_2)P(X)Ph_2$ (X = O, S) with tetrachloro(pentamethylcyclopentadienyl)tantalum(V) give several new derivatives, $Ta(\eta^5\text{-}C_5Me_5)Cl_3(CH_2)_2PRR'$ and $Ta(\eta^5\text{-}C_5Me_5)Cl_3(CH_2)P(X)Ph_2$. The structural characterization of these compounds is based on ^1H and ^{31}P NMR spectroscopic data.

Introduction

We recently reported[1] the isolation of the first neutral (alkylidenephosphorane)tantalum complexes. Since a number of isomeric forms are possible in much of the ylide chemistry, we sought to explore the extent that tantalum would assume the different known structures. In particular, the difunctionalized anionic ylides of the type $[(CH_2)_2PR_2]^-$ can function as terminal, chelate, or bridging ligands to give the isomeric structures A–D.



Complexes containing alternatively one of these structures have been reported for different metals,[2] and in some cases[3] equilibria between them have been found.

We observed that reactions of neutral (alkylidenephosphorane)tantalum complexes with an excess of the phosphorus ylide did not take place at room temperature and not transylidation but formation of complicated unresolvable mixtures was obtained on heating.

An alternative method to prepare this type of complexes with phosphonium bis(ylide) anions is the reaction of the halide with lithium phosphoylide.[4] Here we report the results obtained in these reactions and the structural study of the products as well as the preparation and characterization of complexes containing the pseudoylide ligand $[(CH_2)P(X)Ph_2]^-$ (X = O, S).[5]

Results and Discussion

The reaction represented in eq 1 was performed by adding n-hexane to an equimolar mixture of the solid

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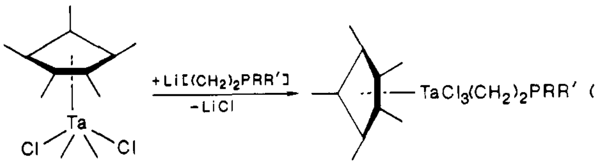
Table I. ^1H and ^{31}P NMR Data for Tantalum(V) Derivatives[a]

	^1H					
complex	Ph	Ta-CH_2	P-Me	Ta-CH_2	C_5Me_5	$^{31}P\{^1H\}$
I monomer		1.83 d [8.52]	0.98 d [13.10]	−0.91 d [11.19]	2.10 s	23.97 s
I dimer		b	0.93 d [13.10]	−0.84 d [11.19]	2.18 s	33.87 s
II monomer	6.99 m, 7.20 m	b	1.33 d [12.79]	−0.24 to −0.46	2.10 s	32.02 s
II dimer	6.99 m, 7.20 m	b	1.37 d [12.83]	−0.24 to −0.46	2.18 s	41.00 s
III	6.90 m, 7.15 m	2.53 d [8.46]		0.10 d [11.47]	2.10 s	35.07 s
IV	6.95 m, 7.39 m	2.91 d [4.98]			2.24 s	73.30 s
V	6.94 m	3.01 d [7.04]			2.28 s	58.13 s

[a] All data NMR in C_6D_6 solution. Chemical shifts in δ in ppm. $^2J_{P-H}$ in brackets in Hz. [b] Overlapped.

lithium derivative prepared as reported[4] and the tantalum complex.

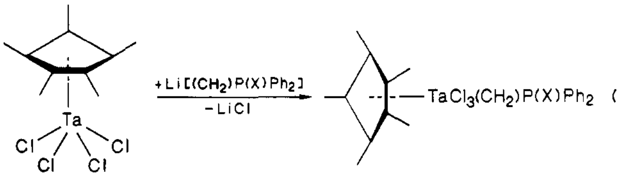


(1)

I: R = R' = Me
II: R = Me, R' = Ph
III: R = R' = Ph

Similar complexes were obtained by using $Li[(CH_2)P(X)Ph_2]$ (X = O, S)[5] instead of the anionic ylides mentioned above. The substitution of the ylide system $P{=}CH_2$ by a σ-donor atom ($P{=}X$) preserves the nature of the σ-alkyl group at the other extreme of the bidentate ligand which can then be used as a reference for structural purposes.

The addition of the tantalum complex to a 2:1 Et_2O/THF solution of the lithium derivative in a molar ratio of 1:1 produces an immediate color change from yellow to orange according to eq 2.



(2)

IV: X = O
V: X = S

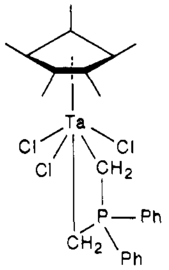
Very air-sensitive, orange, microcrystalline solids were obtained by evaporation and cooling, which are identified by their analytical composition. They are easily hydrolyzed in the presence of traces of water to give $(X)PMePh_2$ and the reported[6] $[Ta(\eta^5\text{-}C_5Me_5)Cl_2(\mu\text{-}OH)]_2(\mu\text{-}O)$.

Complex ^1H NMR spectra are observed for complexes I and II whereas III shows a simple spectrum that consists of one singlet due to the methyl ring protons at δ 2.10 ppm, two doublets assignable to the methylene ylide protons at δ 2.53 ppm ($^2J_{P-H}$ = 8.46 Hz) and δ 0.10 ppm ($^2J_{P-H}$ = 11.47 Hz), and two multiplets at δ 6.90 and 7.15 ppm due to the phenyl protons. The ^{31}P NMR spectrum shows one singlet at δ 35.07 ppm.

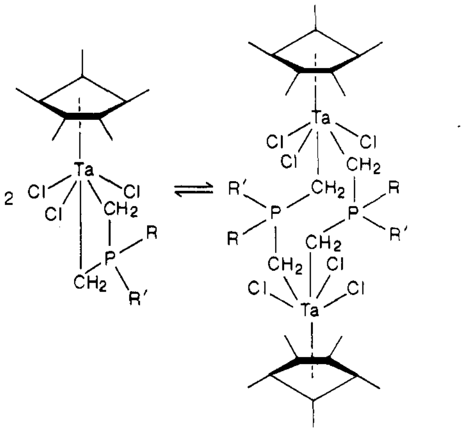
These data suggest that III most likely assumes structure A because it is very well-known[3] that ylide ligands with bulkier R substituents must favor the formation of chelated monomers.

The high-field doublet most likely is due to the methylene hydrogen atoms trans to the more electron-donating pentamethylcyclopentadienyl group whereas the lower field doublet has to correspond to the equatorial methylene hydrogen atoms trans to the chlorine. Relative coupling constants also are in agreement with this assignment.

Chart I. Monomer for R = R' = Ph (III)



Scheme I. Isomers for R = R' = Me (I) and R = Me, R' = Ph (II)



(3)

The ^{31}P NMR spectra for both complexes I and II show two singlets that suggest the presence of two different isomers as illustrated in Scheme I.

Each component has only one ^{31}P resonance so that in the case of the dimer with two ylide bridges the two phosphorus atoms must be equivalent. The ^1H NMR spectrum of complex I is the superposition of these two isomers in a relative ratio that depends on the solvent, the time, and the temperature in such a way that it is not possible to obtain only one of the isomers by changing any of these factors. Each of both components shows one singlet for C_5Me_5 protons, two doublets due to methylene protons, and a third doublet due to methyl phosphorus protons (see Table I).

A detailed study of the relative intensity of ^1H resonances and their dependence on temperature permits a structural assignment. We observe that each component has to contain (i) one or two equivalent phosphorus atoms and therefore only one doublet due to equivalent methyl phosphorus protons, (ii) one or two equivalent pentamethylcyclopentadienyl rings giving rise to only one singlet, and (iii) two nonequivalent methylene groups giving rise to two doublets with different chemical shifts and coupling constants.

Only one of the seven possible isomeric dimers accomplishes these three conditions, just the one represented in

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[6] Jernakoff, P.; de Meric de Bellefon, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* 1987, 6, 1362.

Scheme I, and therefore the other component in the equilibrium (eq 3) has to be the same monomer illustrated in Chart I for complex III.

It is well-known[3,7] that the dissociation of the dimer into the monomer is favored by increasing temperature, so that those resonances intensified at lower temperatures must be assigned to the dimer and the others to the monomer as shown in Table I.

A similar behavior is also observed in the ^{1}H NMR spectrum of complex II for which more than two partially overlapping doublets are observed for the methylene protons of each component due the inequivalence of both diastereotopic CH_2 protons.

The bonding situation can be represented as a contribution of two different canonical forms, which contain a planar phosphometallacycle[8] and a pseudophosphoallyl group, the first most likely prevailing over the second.

It is also important to note that the lower and different coupling constants in relation with that observed for P–Me protons indicate a delocalization polarized by a different trans effect on both methylene groups.

Complexes IV and V show ^{31}P NMR spectra that contain one singlet at δ 73.30 ppm and one at δ 58.13 ppm, respectively.

The ^{1}H NMR spectra show one singlet due to pentamethylcyclopentadienyl protons, one doublet due to the methylene protons of the ligand, and two multiplets for the phenyl protons. The chemical shifts of the methyl ring protons are intermediate between those observed for neutral[1] and anionic bidentate ylides. The chemical shifts observed for the methylene protons at δ 2.91 and 3.01 ppm with $^2J_{P-H}$ = 4.98 and 7.04 Hz suggest the location of this group in the equatorial plane.

Experimental Section

Materials and Measurements. All reactions of air- and moisture-sensitive materials were performed under a nitrogen or argon atmosphere employing standard Schlenk techniques. Solids and solutions were manipulated under argon in a Vacuum Atmospheres glovebox equipped with a HE-63-P dri-train.

The following solvents were dried, freshly distilled, and degassed prior use: diethyl ether and THF (sodium–benzophenone), toluene (sodium), and *n*-hexane (calcium hydride).

MeI, MeLi, PMe_3, PMe_2Ph, $PMePh_2$, and $(X)PPh_3$ (X = O, S) were used as pure chemicals without further purification. $Li[(CH_2)_2PRR']$ (R = R′ = Me = Ph; R = Me, R′ = Ph) and $Li[(CH_2)P(X)Ph_2]$ (X = O, S) reagents were prepared and isolated as described[4,5] from MeLi and the appropriate phosphonium salt in a Et_2O/THF mixture (2:1) as the solvent, then weighed out in the glovebox, and added to the starting tantalum complex.

$Ta(\eta^5\text{-}C_5Me_5)Cl_4$ was prepared by using reported methods.[9]

Infrared spectra were recorded as Nujol mulls (4000–200 cm^{-1}) between polyethylene films on a Perkin-Elmer 599 spectrometer. ^{1}H and ^{31}P NMR spectra were measured on a Varian FT-80 A instrument. Chemical shifts are reported in δ units (positive chemical shifts to a higher frequency) relative to tetramethylsilane (TMS) and phosphoric acid (H_3PO_4).

C and H elemental analyses were carried out on a Perkin-Elmer 240 B microanalyzer.

Preparation of $Ta(\eta^5\text{-}C_5Me_5)Cl_3(CH_2)_2PRR'$ (I and II). *n*-Hexane (35 mL) was added to a $Li[(CH_2)_2PRR']$ (1.25 mmol) and $Ta(\eta^5\text{-}C_5Me_5)Cl_4$ (0.57 g, 1.24 mmol) solid mixture. After being stirred for 2 h, the suspension was filtered and the solid was extracted with cold toluene (3 × 20 mL). The solution was concentrated till ca 15 mL, *n*-hexane (30 mL) added, and the mixture cooled to −40 °C to give a brown-red (I, R = R′ = Me) or an orange (II, R = Me, R′ = Ph) crystalline solid.

I: yield, 60% (0.3 g); IR (Nujol mull) 1293 (m), 1283 (m), 1018 (m), 967 (vs), 820 (w), 759 (w), 674 (w), 507 (s), 440 (w), 272 (br, vs) cm^{-1}. ^{1}H NMR (δ (ppm) in C_6D_6): monomer, 2.10 (s, 15 H, C_5Me_5), −0.91 (d, 2 H, $^2J_{P-H}$ = 11.19 Hz, Ta–CH_2), 0.98 (d, 6 H, $^2J_{P-H}$ = 13.10 Hz, P–Me), 1.83 (d, 2 H, $^2J_{P-H}$ = 8.52 Hz, Ta–CH_2); dimer, 2.18 (s, 30 H, C_5Me_5), −0.84 (d, 4 H, $^2J_{P-H}$ = 11.19 Hz, Ta–CH_2), 0.93 (d, 12 H, $^2J_{P-H}$ = 13.10 Hz, P–Me). ^{31}P NMR (gated decoupled; δ (ppm) in C_6D_6): monomer, 23.97 (s, $(CH_2)_2PMe_2$); dimer, 33.87 (s, $(CH_2)_2PMe_2$). Anal. Calcd for $TaCl_3PC_{14}H_{25}$: C, 32.85; H, 4.92. Found: C, 32.65; H, 4.82.

II: yield, 51% (0.28 g); IR (Nujol mull) 1113 (vs), 1017 (w), 991 (m), 954 (w), 942 (w), 922 (w), 884 (br), 874 (m), 812 (m), 750 (vs), 695 (m), 515 (s), 452 (w), 347 (w), 300–278 (vs) cm^{-1}. ^{1}H NMR (δ (ppm) in C_6D_6): monomer, 2.10 (s, 15 H, C_5Me_5), −0.24 to −0.46 (2 H, Ta–CH_2), 1.33 (d, 3 H, $^2J_{P-H}$ = 12.79 Hz, P–Me), 6.99–7.20 (m, 5 H, Ph); dimer, 2.18 (s, 30 H, C_5Me_5), −0.24 to −0.46 (4 H, Ta–CH_2), 1.37 (d, 6 H, $^2J_{P-H}$ = 12.83 Hz, P–Me), 6.99–7.20 (m, 10 H, Ph). ^{31}P NMR (gated decoupled; δ (ppm) in C_6D_6): monomer, 32.02 (s, $(CH_2)_2PMePh$); dimer, 41.00 (s, $(CH_2)_2PMePh$). Anal. Calcd for $TaCl_3PC_{19}H_{27}$: C, 39.77; H, 4.74. Found: C, 39.50; H, 4.90.

Preparation of $Ta(\eta^5\text{-}C_5Me_5)Cl_3(CH_2)_2PPh_2$ (III). $Ta(\eta^5\text{-}C_5Me_5)Cl_4$ (0.74 g, 1.62 mmol) was added to a suspension of $Li[(CH_2)_2PPh_2]$ in toluene (30 mL) to −40 °C and the mixture stirred for 5 h. The yellow suspension obtained was filtered, and the solution was concentrated ca. 15 mL and cooled to −40 °C to give a brown-yellow microcrystalline solid of III.

III: yield 67% (0.68 g); IR (Nujol mull) 1112 (vs), 1020 (m), 980 (m), 940 (m), 842 (m), 811 (m), 743 (vs), 691 (s), 531 (vs), 476 (m), 344 (m), 297 (m), 272 (s) cm^{-1}; ^{1}H NMR (δ (ppm) in C_6D_6) 2.10 (s, 15 H, C_5Me_5), 0.10 (d, 2 H, $^2J_{P-H}$ = 11.47 Hz, Ta–CH_2), 2.53 (d, 2 H, $^2J_{P-H}$ = 8.46 Hz, Ta–CH_2), 6.90–7.15 (m, 10 H, Ph); ^{31}P NMR (gated decoupled; δ (ppm) in C_6D_6 35.07 (s, $(CH_2)_2PPPh_2$). Anal. Calcd for $TaCl_3PC_{24}H_{29}$: C, 45.74; H, 4.59. Found: C, 45.94; H, 4.39.

Preparation of $Ta(\eta^5\text{-}C_5Me_5)Cl_3(CH_2)P(X)Ph_2$ (IV and V). $Ta(\eta^5\text{-}C_5Me_5)Cl_4$ (0.67 g, 1.46 mmol) was added to a solution of $Li[(CH_2)P(X)Ph_2]$ (1.46 mmol) in Et_2O/THF (2:1) and the mixture stirred (X = O, 48 h; X = S, 14 h). The solution was filtered and evaporated to dryness, and the residue was extracted with toluene (3 × 15 mL). The toluene solution was concentrated to ca. 20 mL, *n*-hexane (10 mL) was added, and the mixture was cooled overnight to −40 °C; orange microcrystalline IV and V were isolated.

IV: yield 45% (0.42 g); IR (Nujol mull) 1128 (s), 1075 (w), 1028 (w), 999 (w), 969 (vs), 924 (m), 882 (w), 865 (m), 762–752 (br, vs), 702 (s), 599 (vs), 522 (m), 509 (s), 467 (w), 429 (w), 405 (w), 357 (m), 319 (s), 287 (s) cm^{-1}; ^{1}H NMR (δ (ppm) in C_6D_6) 2.24 (s, 15 H, C_5Me_5), 2.91 (d, 2 H, $^2J_{P-H}$ = 4.98 Hz, Ta–CH_2), 6.95–7.39 (m, 10 H, Ph); ^{31}P NMR (gated decoupled; δ (ppm) in C_6D_6) 73.30 (s, $(CH_2)P(O)Ph_2$). Anal. Calcd for $TaCl_3POC_{23}H_{27}$: C, 43.31; H, 4.26. Found: C, 42.89; H, 4.21.

V: yield, 34% (0.40 g); IR (Nujol mull) 1106 (s), 1020 (m), 1000 (w), 959 (m), 940 (w), 929 (w), 890 (w), 833 (m), 750 (vs), 700 (vs), 649 (w), 615 (w), 590 (vs), 505 (s), 477 (m), 458 (m), 352 (m), 300 (s), 280 (s) cm^{-1}; ^{1}H NMR (δ (ppm) in C_6D_6) 2.28 (s, 15 H, C_5Me_5), 3.01 (d, 2 H, $^2J_{P-H}$ = 7.04 Hz, Ta–CH_2), 6.94 (m, 10 H, Ph); ^{31}P NMR (gated decoupled; δ (ppm) in C_6D_6) 58.13 (s, $(CH_2)P(S)Ph_2$). Anal. Calcd for $TaCl_3PSC_{23}H_{27}$: C, 42.25; H, 4.16. Found: C, 42.65; H, 4.17.

Acknowledgment. We wish to thank CICYT for financial support (ref. PD 86-0093).

Registry No. I (monomer), 120744-00-5; I (dimer), 120744-01-6; II (monomer), 120744-02-7; II (dimer), 120744-03-8; III, 120744-04-9; IV, 120744-05-0; V, 120744-06-1; $Ta(\eta^5\text{-}C_5Me_5)Cl_4$, 71414-47-6; $Li[(CH_2)_2PMe_2]$, 21752-68-1; $Li[(CH_2)_2MePh]$, 59983-61-8; $Li[(CH_2)_2Ph_2]$, 59983-62-9; $Li[(CH_2)P(O)Ph_2]$, 23182-99-2; $Li[(CH_2)P(S)Ph_2]$, 52101-86-7.

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