

(Methylenephosphoranyl)methyl, phosphinylmethyl, and phosphinothioylmethyl complexes of tantalum

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Organometallics, 1989, 8 (7), 1604-1606 • DOI: 10.1021/om00109a004 • Publication Date (Web): 01 May 2002

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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 CH₄ 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(η^5 -C₅H₅)(CO)₃(N₂) and V(η^5 -C₅H₅)(CO)_{4-n}(C₂H₄)_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(η^5 -C₅H₅)(CO)₄ suggest that the bis(ethylene) species exists as the *trans* isomer, i.e. *trans*-V(η^5 -C₅H₅)(CO)₂(C₂H₄)₂. Although kinetic studies¹⁴ and quantum yield measurements⁴ favored dissociative paths for the thermal and photochemical substitution reactions of V(η^5 -C₅H₅)(CO)₄, an associative pathway could not be ruled out. The possibility that a C₅H₅ 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(η^5 -C₅H₅)(CO)₂ in a CO matrix.³¹ It is proposed, therefore, that the species formed on long wavelength photolysis of V(η^5 -C₅H₅)(CO)₄ in all matrices

(Ar, CH₄, N₂, CO) is the η^3 -C₅H₅ species V(η^3 -C₅H₅)(CO)₄ and that in a CO matrix this species may add a further CO ligand to give V(η^3 -C₅H₅)(CO)₅ (18-electron species) or V(η^1 -C₅H₅)(CO)₅ (16-electron species) depending on the electronic requirements for a filled shell versus steric crowding. The evidence in favor of ring-slippage η^3 -C₅H₅ species suggests that the possible contribution of S_N2 pathways in solution thermal and photochemical reactions should be reevaluated for V(η^5 -C₅H₅)(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(η^5 -C₅H₅)(CO)₄, 12108-04-2; V(η^3 -C₅H₅)(CO)₄, 120610-57-3; V(η^5 -C₅H₅)(CO)₃, 120610-58-4; V(η^5 -C₅H₅)(CO)₂, 120610-59-5; V(η^5 -C₅H₅)(CO), 120610-60-8; V(η^5 -C₅H₅)(CO)₃(N₂), 120610-61-9; V(η^5 -C₅H₅)(CO)₃(C₂H₄), 120610-62-0; V(η^5 -C₅H₅)(CO)₂(C₂H₄)₂, 120610-63-1; V(η -C₅H₅)(CO)₅, 120636-93-3; V(η^5 -C₅H₅)(¹²CO)₃(¹³CO), 99629-80-8; V(η^5 -C₅H₅)(¹²CO)₂(¹³CO)₂ (isomer 1), 120610-64-2; V(η^5 -C₅H₅)(¹²CO)₂(¹³CO)₂ (isomer 2), 120707-79-1; V(η^5 -C₅H₅)(¹²CO)(¹³CO)₃, 120610-65-3; V(η^5 -C₅H₅)(¹³CO)₄, 120610-66-4; V(η^5 -C₅H₅)(¹²CO)₂(¹³CO), 120610-67-5; V(η^5 -C₅H₅)(¹²CO)(¹³CO)₂, 120610-68-6; V(η^5 -C₅H₅)(¹³CO)₃, 120610-69-7; V(η^5 -C₅H₅)(¹²CO)(¹³CO), 120610-70-0; V(η^5 -C₅H₅)(¹³CO)₂, 120610-71-1; V(η^5 -C₅H₅)(¹³CO), 120610-72-2.

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

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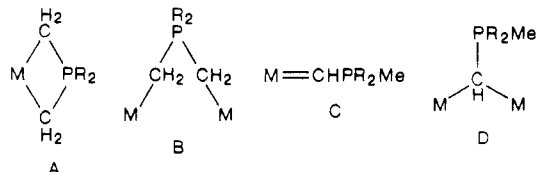
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Received July 25, 1988

The reactions of lithium salts of the anionic ylides (CH₂)₂PRR' (R = R' = Me; R = Me, R' = Ph; R = R' = Ph) and pseudoylides (CH₂)P(X)Ph₂ (X = O, S) with tetrachloro(pentamethylcyclopentadienyl)-tantalum(V) give several new derivatives, Ta(η^5 -C₅Me₅)Cl₃(CH₂)₂PRR' and Ta(η^5 -C₅Me₅)Cl₃(CH₂)P(X)Ph₂. The structural characterization of these compounds is based on ¹H and ³¹P NMR spectroscopic data.

Introduction

We recently reported¹ the isolation of the first neutral (alkylidene-phosphorane)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 [(CH₂)₂PR₂]⁻ 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 cases³ equilibria between them have been found.

We observed that reactions of neutral (alkylidene-phosphorane)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 [(CH₂)P(X)Ph₂]⁻ (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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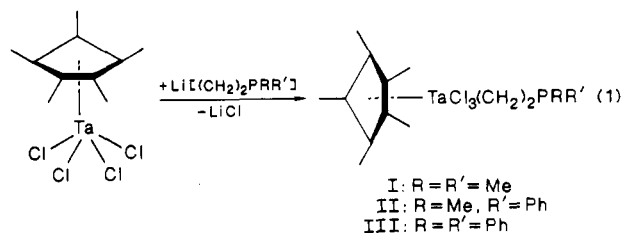
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Table I. ¹H and ³¹P NMR Data for Tantalum(V) Derivatives^a

complex	¹ H					³¹ P{ ¹ H}
	Ph	Ta-CH ₂	P-Me	Ta-CH ₂	C ₅ Me ₅	
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		<i>b</i>	0.93 d [13.10]	-0.84 d [11.19]	2.18 s	33.87 s
II monomer	6.99 m, 7.20 m	<i>b</i>	1.33 d [12.79]	-0.24 to -0.46	2.10 s	32.02 s
II dimer	6.99 m, 7.20 m	<i>b</i>	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

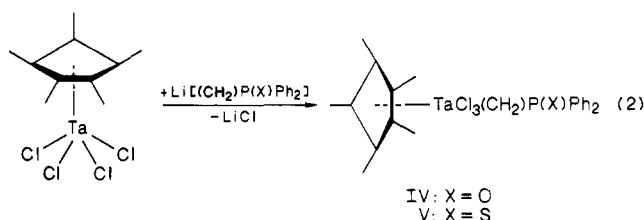
^aAll data NMR in C₆D₆ solution. Chemical shifts in δ in ppm. ²J_{P-H} in brackets in Hz. ^bOverlapped.

lithium derivative prepared as reported⁴ and the tantalum complex.



Similar complexes were obtained by using Li[(CH₂)P(X)Ph₂] (X = O, S)⁵ instead of the anionic ylides mentioned above. The substitution of the ylide system P=CH₂ 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 Et₂O/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.



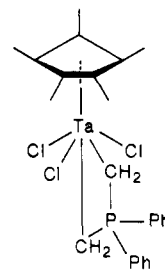
Very air-sensitive, orange, microcrystalline solids were obtained by evaporation and cooling, which are identified by their analytical composition. They are easily hydrolyzed in the presence of traces of water to give (X)PMePh₂ and the reported⁶ [Ta(η⁵-C₅Me₅)Cl₂(μ-OH)]₂(μ-O).

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 ³¹P NMR spectrum shows one singlet at δ 35.07 ppm.

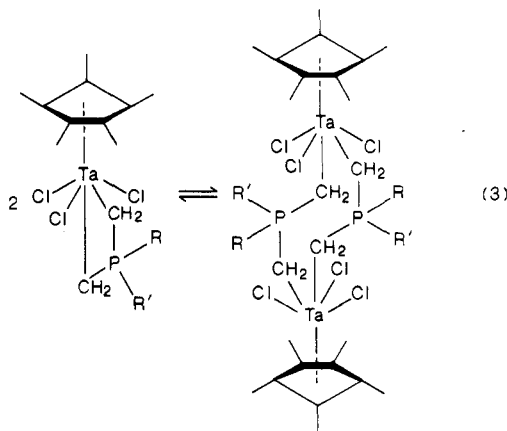
These data suggest that III most likely assumes structure A because it is very well-known³ that ylide ligands with bulkier R substituents must favor the formation of chelated monomers.

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

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



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



constants also are in agreement with this assignment.

The ³¹P 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 ³¹P 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 C₅Me₅ 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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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 ¹H 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 CH₂ protons.

The bonding situation can be represented as a contribution of two different canonical forms, which contain a planar phosphometallacycle⁸ 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 ³¹P NMR spectra that contain one singlet at δ 73.30 ppm and one at δ 58.13 ppm, respectively.

The ¹H NMR spectra show one singlet due to penta-methylcyclopentadienyl 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 neutral¹ 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, PMe₃, PMe₂Ph, PMePh₂, and (X)PPh₃ (X = O, S) were used as pure chemicals without further purification.

Li[(CH₂)₂PRR'] (R = R' = Me = Ph; R = Me, R' = Ph) and Li[(CH₂)₂P(X)Ph₂] (X = O, S) reagents were prepared and isolated as described^{4,5} from MeLi and the appropriate phosphonium salt in a Et₂O/THF mixture (2:1) as the solvent, then weighed out in the glovebox, and added to the starting tantalum complex.

Ta(η⁵-C₅Me₅)Cl₄ 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. ¹H and ³¹P 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 (H₃PO₄).

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

Preparation of Ta(η⁵-C₅Me₅)Cl₃(CH₂)₂PRR' (I and II). *n*-Hexane (35 mL) was added to a Li[(CH₂)₂PRR'] (1.25 mmol)

and Ta(η⁵-C₅Me₅)Cl₄ (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. ¹H NMR (δ (ppm) in C₆D₆): monomer, 2.10 (s, 15 H, C₅Me₅), -0.91 (d, 2 H, ²J_{P-H} = 11.19 Hz, Ta-CH₂), 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-CH₂); dimer, 2.18 (s, 30 H, C₅Me₅), -0.84 (d, 4 H, ²J_{P-H} = 11.19 Hz, Ta-CH₂), 0.93 (d, 12 H, ²J_{P-H} = 13.10 Hz, P-Me). ³¹P NMR (gated decoupled; δ (ppm) in C₆D₆): monomer, 23.97 (s, (CH₂)₂PMe₂); dimer, 33.87 (s, (CH₂)₂PMe₂). Anal. Calcd for TaCl₃PC₁₄H₂₅: 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. ¹H NMR (δ (ppm) in C₆D₆): monomer, 2.10 (s, 15 H, C₅Me₅), -0.24 to -0.46 (2 H, Ta-CH₂), 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, C₅Me₅), -0.24 to -0.46 (4 H, Ta-CH₂), 1.37 (d, 6 H, ²J_{P-H} = 12.83 Hz, P-Me), 6.99–7.20 (m, 10 H, Ph). ³¹P NMR (gated decoupled; δ (ppm) in C₆D₆): monomer, 32.02 (s, (CH₂)₂PMePh); dimer, 41.00 (s, (CH₂)₂PMePh). Anal. Calcd for TaCl₃PC₁₉H₂₇: C, 39.77; H, 4.74. Found: C, 39.50; H, 4.90.

Preparation of Ta(η⁵-C₅Me₅)Cl₃(CH₂)₂PPh₂ (III). Ta(η⁵-C₅Me₅)Cl₄ (0.74 g, 1.62 mmol) was added to a suspension of Li[(CH₂)₂PPh₂] 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; ¹H NMR (δ (ppm) in C₆D₆) 2.10 (s, 15 H, C₅Me₅), 0.10 (d, 2 H, ²J_{P-H} = 11.47 Hz, Ta-CH₂), 2.53 (d, 2 H, ²J_{P-H} = 8.46 Hz, Ta-CH₂), 6.90–7.15 (m, 10 H, Ph); ³¹P NMR (gated decoupled; δ (ppm) in C₆D₆) 35.07 (s, (CH₂)₂PPh₂). Anal. Calcd for TaCl₃PC₂₄H₂₉: C, 45.74; H, 4.59. Found: C, 45.94; H, 4.39.

Preparation of Ta(η⁵-C₅Me₅)Cl₃(CH₂)₂P(X)Ph₂ (IV and V). Ta(η⁵-C₅Me₅)Cl₄ (0.67 g, 1.46 mmol) was added to a solution of Li[(CH₂)₂P(X)Ph₂] (1.46 mmol) in Et₂O/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; ¹H NMR (δ (ppm) in C₆D₆) 2.24 (s, 15 H, C₅Me₅), 2.91 (d, 2 H, ²J_{P-H} = 4.98 Hz, Ta-CH₂), 6.95–7.39 (m, 10 H, Ph); ³¹P NMR (gated decoupled; δ (ppm) in C₆D₆) 73.30 (s, (CH₂)₂P(O)Ph₂). Anal. Calcd for TaCl₃POC₂₃H₂₇: 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; ¹H NMR (δ (ppm) in C₆D₆) 2.28 (s, 15 H, C₅Me₅), 3.01 (d, 2 H, ²J_{P-H} = 7.04 Hz, Ta-CH₂), 6.94 (m, 10 H, Ph); ³¹P NMR (gated decoupled; δ (ppm) in C₆D₆) 58.13 (s, (CH₂)₂P(S)Ph₂). Anal. Calcd for TaCl₃PSC₂₃H₂₇: 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(η⁵-C₅Me₅)Cl₄, 71414-47-6; Li[(CH₂)₂PMe₂], 21752-68-1; Li[(CH₂)₂MePh], 59983-61-8; Li[(CH₂)₂Ph₂], 59983-62-9; Li[(CH₂)₂P(O)Ph₂], 23182-99-2; Li[(CH₂)₂P(S)Ph₂], 52101-86-7.

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