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Early transition-metal complexes of α-keto-stabilized phosphorus ylides[†]

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The complexation behaviour of the *α*-keto-stabilized phosphorus ylides $Ph_3P{=}CHC(O)R$ (R = Ph, Me) towards the early transition metal ions titanium(IV), zirconium(IV) and niobium(III) was investigated. The complex $[Ph_3P{=}CHC(Ph)O]TiBr_2(NMe_2)_2$ was obtained from the reaction of the phosphonium bromide $[Ph_3PCH_2C(O)Ph]Br$ with $Ti(NMe_2)_4$. The crystal structure of this complex is discussed. It is frequently observed that the complex formed from the ylide with the early transition metal is very unstable (not isolable) and stabilizes by migration of one NMe_2 group from the starting metal complex to the ylide. Thus the reaction of $Ph_3P{=}CHC(O)Me$ with $Ti(NMe_2)_4$ provides an access to the novel ylide $Ph_3P{=}CHC(NMe_2){=}CH_2$. Niobium complexes of the *α*-keto-stabilized phosphorus ylides $Ph_3P{=}CHC(O)R$ (R = Ph, Me) were obtained by reacting these ylides with $NbCl_3(TMS{—}C{\equiv}C{—}Ph)\cdot DME$ (TMS, trimethylsilyl; DME, dimethoxyethane) in CH_2Cl_2. A binuclear structure could be confirmed by X-ray crystal structure analysis. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: *α*-keto-stabilization; phosphorus ylides; early transition metals; titanium; zirconium; niobium

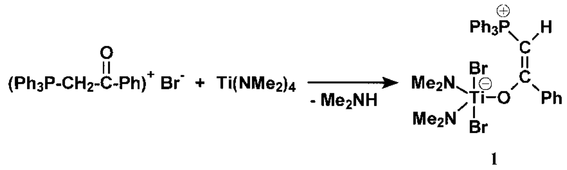
INTRODUCTION

The search for non-metallocene catalysts in olefin polymerization is a field of extensive research activities.[1] Phosphorus ylide complexes are well known.[2] The nickel(II) complex $[Ph_2PCHC(Ph)O]$-$NiPh(PPh_3)$, neither displaying an ylidic ligand nor belonging to the metallocenes, was obtained by Keim *et al.* from the reaction of the ylide $Ph_3P{=}CHC(O)Ph$ with $Ni(cod)_2$ (COD = cyclooctadiene).[3] It was successfully used in the Shell Higher Olefin Process (SHOP).[4] α-Keto-stabilized phosphorus ylides are able to act as ambidentate ligands (C vs O coordination). Whereas complexes of α-keto-stabilized phosphorus ylides with late transition-metal ions are thoroughly investigated, there are only a few examples of such complexes with early transition metals.[5,6] We describe here an investigation into the complexation behaviour of the phosphorus ylides $Ph_3P{=}CHC(O)R$ (R = Ph, Me) toward early transition-metal ions.

RESULTS AND DISCUSSION

From the reaction of the phosphonium bromide $[Ph_3P{—}CH_2C(O)Ph]Br$[7] with $Ti(NMe_2)_4$ in a 2:1 ratio in tetrahydrofuran (THF) the complex $[Ph_3P{=}CHC(Ph)O]TiBr_2(NMe_2)_2$ (**1**) was obtained (Scheme 1). Bromination of the metal takes place simultaneously to the complexation.

The crystal structure of **1**, represented in Fig. 1, shows the strongly distorted trigonal-bipyrimidal geometry at the titanium [Br1-Ti-Br2, 161.43(4) °]. The phosphorus ylide, existing in a cisoid arrangement, employs the carbonyl oxygen to bind to the metal centre. The elongation of the P–C(methine) bond in **1** relative to the free ylide supports the localization of the positive charge at the phosphorus



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Scheme 1

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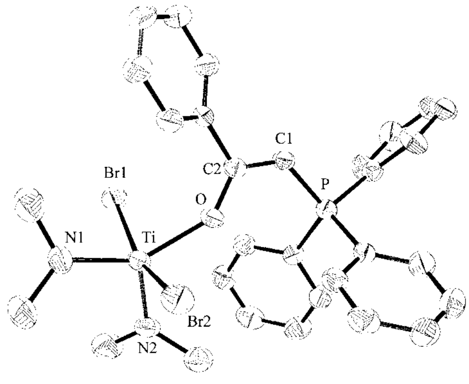


Figure 1 Crystal structure of **1**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): C1–C2 1.355(7), C1–P 1.746(5), C2–O 1.303(3), Ti–O 1.978(3), Ti–N1 1.854(4), Ti–N2 1.876(5), Ti–Br1 2.581(1), Ti–Br2 2.610(1); N2-Ti-N1 106.0(2), N2-Ti-O 110.3(2), N1-Ti-O 143.6(2), Br1-Ti-Br2 161.43(4), N1-Ti-Br1 90.48(14), Ti-O-C2 144.6(3), O-C2-C1 123.0(5), C2-C1-P 128.7(4).

atom. The C1–C2 bond length [1.355(7) Å] is in the range of a C–C double bond. The lengthening of the C–O bond is comparable with those in $[Ph_3P{=}CHC(Me)O]TiCl_4(THF)$[5] and $[Ph_3PCHC(C_3H_2NS)O]NbCl_3(nPrC{\equiv}CPh)$[6] and is consistent with the resonance formula as given in Scheme 1 (Table 1).

IR and NMR spectroscopy are suitable indicators for judging the bonding mode of the α-keto ylides.[5] A decreasing carbonyl streching frequency in the IR spectrum of the complex, resulting from major contributions from the resonance structure Ph_3P^+—CH=C(Ph)—O^-, confirms that the ligand is bound through the carbonyl oxygen (Table 2).

As expected, the ^{31}P NMR signal for the O-coordinated ylide in the titanium complex **1** (14.7 ppm) is observed at slightly higher field compared with the free ylide (17.6 ppm). The ^2J(H,P) value (21 Hz) is smaller than for the uncomplexed ylide (26 Hz). This is in accordance with the general trend of the coupling constants: free ylide > O-coordinated ylide > ylide hydrohalide salt (phosphonium salt) > C-coordinated ylide.[5]

We often found that the complexes of the ylides generated with early transition metals are very unstable and not isolable. These intermediates undergo consecutive reactions in which one NMe_2 group is transferred from the starting metal complex to the ylide. Such transfer reactions were observed for the systems $Ph_3P{=}CHC(O)Me/Ti(NMe)_4$ and $Ph_3P{=}CHC(O)Ph/Zr(NMe)_4$ (Schemes 2 and 3). The organic products **2** and **3** were characterized by elemental analysis, NMR

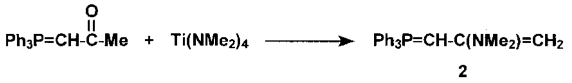
Table 1 Comparison of selected bond lengths in **1** with $Ph_3PCHC(O)Ph$ (Ref. 12), $[Ph_3PCHC(Me)O]TiCl_4(THF)$ (Ref. 5) and $[Ph_3PCHC(C_3H_2NS)O]NbCl_3(nPrC{\equiv}CPh)$ (Ref. 6a)

Compound	P $\overline{\cdots}$ CH	PCH $\overline{\cdots}$ C	C $\overline{\cdots}$ O
$Ph_3PCHC(O)Ph$	1.711	1.390	1.255
$[Ph_3PCHC(O)Ph]TiBr_2(NMe_2)_2$ (**1**)	1.746(5)	1.355(7)	1.303(5)
$[Ph_3PCHC(Me)O]TiCl_4(THF)$	1.774(7)	1.333(9)	1.332(8)
$[Ph_3PCHC(C_3H_2NS)O]NbCl_3(nPrC{\equiv}CPh)$	1.755(5)	1.370(7)	1.289(7)

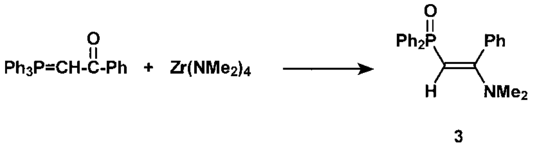
Table 2 Selected IR data for the free ylides and their complexes

Compound	ν_{CO} (cm^{-1})	$\nu_{C\equiv C}$ (coord.) (cm^{-1})
$NbCl_3(TMS\text{-}C{\equiv}C\text{-}Ph)(DME)$[a]		1657
$Ph_3P{=}CHC(O)Ph$[b]	1526	
$[Ph_3P{=}CHC(Ph)O]TiBr_2(NMe_2)_2$ (**1**)	1510	
$\{[Ph_3P{=}CHC(Ph)O]NbCl_3(TMSC{\equiv}CPh)\}_2$ (**4**)	1528	1675
$Ph_3P{=}CHC(O)Me$[b]	1539	
$\{[Ph_3P{=}CHC(Me)O]NbCl_3(TMSC{\equiv}CPh)\}_2$ (**5**)	1526	1667 and 1718[c]

[a] Ref. 9.
[b] Ref. 7.
[c] Two isomers.



Scheme 2



Scheme 3

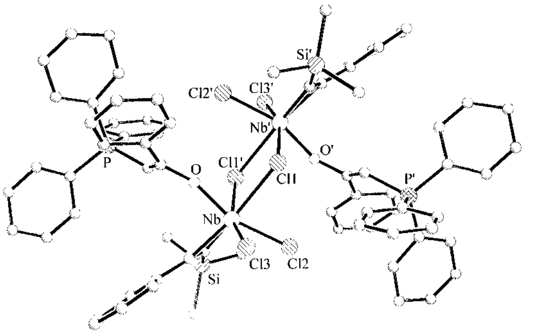


Figure 2 Crystal structure of **4**. Hydrogen atoms are omitted for clarity.

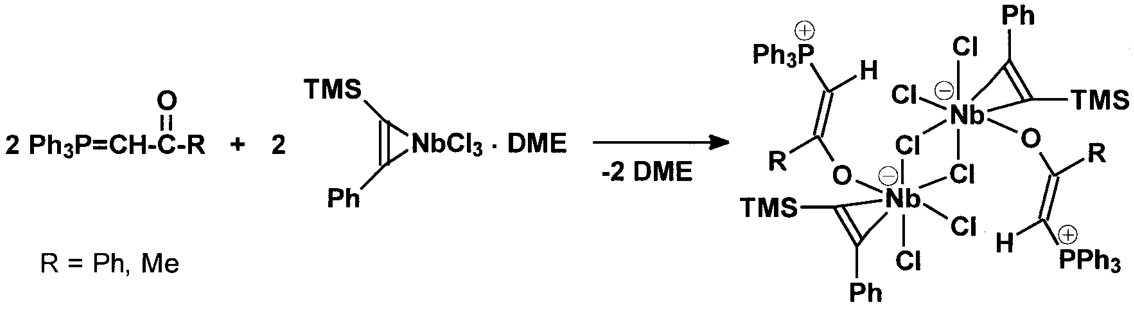
and MS. Their structures could also be confirmed by X-ray structure analyses.

The modified ylide $Ph_3P{=}CHC(NMe_2){=}CH_2$ (**2**) obtained is easily accessible in this way (Scheme 2) and can readily be complexed with late transition metals. These compounds are the topic of further investigations which are in progress.

Niobium complexes of the α-keto-stabilized phosphorus ylides $Ph_3P{=}CHC(O)R$ (R = Ph, Me) were obtained by the reaction of these ylides with $NbCl_3(TMS{-}C{\equiv}C{-}Ph){\cdot}DME$[9] (TMS, trimethylsilyl; DME, dimethoxyethane) in CH_2Cl_2 (Scheme 4). An equilibrium of two isomers could be found in solution, detected in the ^{31}P NMR spectra. Characterization of the two isomers proved to be difficult; therefore a discussion in detail is not possible.

The binuclear structure of **4** was confirmed by an X-ray crystal structure analysis. Due to the insufficient quality of the single crystals the crystal structure of **4** does not allow an extensive discussion of bonding lengths and angles. The coordination geometry can be described as a distorted octahedron for each niobium atom (Fig. 2).

One metal centre is complexed by two terminal chlorine atoms, the alkyne, the O-bound ylide and two chlorine atoms, which bridge the metal centres. Surprisingly the ylide adopts the transoid arrangement in the solid state. The η^2-coordinated alkyne was not displaced. This observation is confirmed in the IR spectra. The absorption for the coordinated alkyne appears at 1675 cm^{-1} for **4** and 1667 cm^{-1} (1718 cm^{-1} for the second species) for **5** (Table 2). The free alkyne shows a band for the C–C triple bond at 2160 cm^{-1}. The carbonyl streching frequency in **5** is decreased in comparison with the free ylide (Table 2). This confirms that the $Ph_3P{=}CHC(O)Me$ in **5** is bound through the carbonyl oxygen as $Ph_3P{=}CHC(O)Ph$ is in **4**. Unexpectedly



4 (R = Ph)
5 (R = Me)

Scheme 4

the ν(CO) absorption in **4** reveals no significant change with respect to the free ylide. In the NMR spectra the complex **5** shows a comparable behaviour to complex **4**; therefore we suppose it has a corresponding molecular structure.

EXPERIMENTAL

Benzoyltriphenylphosphonium bromide,[7] benzoyltriphenylphosphorane,[7] tetrakis(dimethylamino) zirconium(IV)[8] and [1-phenyl-2-(trimethylsilyl) acetylene]niobium(III) chloride[9] were prepared according to literature procedures. All other reagents were obtained commercially and used as supplied. All operations with air-sensitive materials were carried out under an inert atmosphere (argon) using Schlenk techniques. Before use, solvents were dried and freshly distilled under argon. NMR spectra were recorded on a Bruker ARX 400 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to the solvent resonances and reported relative to tetramethylsilane. Melting points were determined in sealed capillaries on a Büchi 535 apparatus. Elemental analyses were performed with a Leco CHNS-932 elemental analyser. The IR spectra were recorded on a Nicolet Magna 550 spectrometer. X-ray data of compounds **1**, **2**, **3** and **4** were collected on a STOE-IPDS diffractometer using graphite monochromated Mo-K$_\alpha$ radiation. The structures were solved by direct methods (*SHELXS-86*)[10] and refined by full-matrix least-squares techniques against F^2 (*SHELXL-93*).[11] XP (Siemens Analytical X-ray Instruments) was used for structure representations. The crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 133821 (for compound **2**), CCDC 133822 (for compound **3**), CCDC 133823 (for compound **1**) and CCDC 133824 (for compound **4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 12223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

$[Ph_3P{=}CHC(Ph)O]TiBr_2(NMe_2)_2$ (1)

$[Ph_3PCH_2C(O)Ph]Br$ (2.77 g, 6 mmol) was suspended in 20 ml of THF, $Ti(NMe_2)_4$ (700 μl, 3 mmol) was added and the solution turned dark red while all the solids dissolved. After stirring for an hour the solution was filtered, concentrated *in vacuo* and layered with ether. At −30 °C red crystals, contaminated with a yellow powder, were precipitated. The precipitate was washed with cold THF to yield 1.10 g (48%) of a red crystalline product, m.p. 110 °C.

Analysis: Calcd for $C_{37}H_{41}Br_2N_2OPTi$ (768.41): C, 57.83; H, 5.38; N, 3.65; Found: C, 57.07; H, 5.44; N, 3.63%. ^{1}H NMR (toluene-d_8), δ (ppm): 3.08 (s, 6H, NMe$_2$), 4.32 (d, ^2J(H,P) = 21 Hz, 1H, =CH), 6.90 –7.17 (m, 12H, *m*-Ph, *p*-Ph), 7.65 (m, 6H, *o*-P-Ph), 8.08 (br., 2H, *o*-C-Ph). ^{31}P NMR (toluene-d_8), δ (ppm): 14.7. IR (Nujol), $\tilde{\nu}$ (cm^{-1}): 1510 (carbonyl, coordinated). Crystal data: crystal dimensions 0.5 mm × 0.4 mm × 0.3 mm, dark red prisms, space group $P2_1/c$, monoclinic, a = 13.872(3) Å, b = 13.984(3) Å, c = 19.347(4) Å, β = 105.86(3) °, V = 3610(1) Å^3, Z = 4, ρ_{calcd} =1.414 g cm^{-1}, 10 499 reflections measured of which 5725 were independent of symmetry and 3178 were observed ($I > 2\sigma(I)$), $R1$ = 0.046, wR^2 (all data) = 0.113, 366 parameters.

$Ph_3P{=}CHC(NMe_2){=}CH_2$ (2)

$Ti(NMe_2)_4$ (467 μl, 2 mmol) was added to a suspension of $Ph_3P{=}CHC(O)Me$ (637 mg, 2 mmol) in 20 ml of toluene. The reaction mixture was stirred for two days and then filtered. The filtrate was concentrated to dryness *in vacuo*. The residue was dissolved in ether and stored at −78 °C. An orange–red powder (677 mg, 98%) was isolated by filtration, m.p: 99 °C.

Analysis: Calcd for $C_{23}H_{24}NP$ (345.42): C, 79.98; H, 7.00; N, 4.05; Found: C, 79.80; H, 6.97; N, 3.98%. ^{1}H NMR (C$_6$D$_6$), δ (ppm): 2.17 (dt, ^2J(H,P) = 18.1 Hz, ^4J(H,H) = 1.3 Hz, 1H, =CH), 2.92 (s, 6H, NMe$_2$), 3.57 (br, 2H, =CH$_2$), 7.04 (m, 9H, *m*-Ph, *p*-Ph), 7.82 (m, 6H, *o*-Ph). ^{13}C NMR (C$_6$D$_6$), δ (ppm): 23.3 (^1J(C,P) = 131.8 Hz, ^1J(C,H) = 158 Hz, ^3J(C,H) = 6 Hz, =CH), 41.9 (^1J(C,H) = 133 Hz, NMe$_2$), 73.5 (^3J(C,P) ≈ ^3J(C,H) = 5 Hz, ^1J(C,H) = 155 Hz, =CH$_2$), 128.5 (^3J(C,P) = 11.5 Hz, ^1J(C,H) = 162 Hz, *m*-Ph), 131.0 (^4J(C,P) = 2.4 Hz, ^1J(C,H) = 161 Hz, *p*-Ph), 131.2 (^1J(C,P) = 87.2 Hz, *i*-Ph), 133.4 (^2J(C,P) = 9.6 Hz, ^1J(C,H) = 161 Hz, *o*-Ph), 158.9 (^2J(C,P) = 15.1 Hz, quaternary C). ^{31}P NMR (C$_6$D$_6$), δ [ppm] = 10.5. MS (70 eV) *m/z*: 345 (M$^+$). Crystal data: crystal dimensions 0.3 mm × 0.2 mm × 0.1 mm, orange prisms, space group $P\bar{1}$, triclinic, a = 9.170(2) Å, b = 11.054(2) Å, c = 20.471(4) Å, α = 78.21(3) °, β = 83.39(3) °, γ = 80.61(3) °, V = 1996.9(7) Å^3, Z = 4, ρ_{calcd} = 1.149 g cm^{-1}, 10620 reflections measured of which 5942 were independent of symmetry and 2167 were observed ($I > 2\sigma(I)$), $R1 = 0.050$, wR^2 (all data) = 0.132, 475 parameters.

$Ph_2P(O)CH{=}C(NMe_2)Ph$ (3)

$Ph_3P{=}CHC(O)Ph$ (461 mg, 1 mmol) was suspended in 20 ml of toluene. $Zr(NMe_2)_4$ (268 mg, 1 mmol), dissolved in 10 ml of toluene, was added. The solid immediately dissolved and the solution turned yellow. The reaction mixture was stirred for two days. After filtration the solution was concentrated *in vacuo* and layered with ether. At −30 °C a yellow, crystalline material was obtained, yield 52 mg (15%), m.p. 153 °C.

Analysis: Calcd for $C_{22}H_{22}NOP$ (347.40): C, 76.06; H, 6.38; N, 4.03; Found: C, 75.61; H, 6.61; N, 4.02%. ^1H NMR (C_6D_6), δ (ppm): 2.21 (s, 6H, NMe_2), 4.88 (d, ^2J(H,P) = 14 Hz, 1H, =CH), 6.89 (m, 3H, *m*-C-Ph, *p*-C-Ph), 7.01 (m, 6H, *m*-P-Ph, *p*-P-Ph), 7.34 (d, 2H, *o*-C-Ph), 7.93 (dd, 4H, *o*-P-Ph). ^{13}C NMR (C_6D_6), δ (ppm): 39.8 (^1J(C,H) = 137 Hz, NMe_2), 89.1 (^1J(C,H) = 150 Hz, ^1J(C,P) = 125 Hz, =CH), 127.7 (*m*-C-Ph), 127.9 (^3J(C,P) = 11 Hz, *m*-P-Ph), 128.7 (*p*-C-Ph), 129.9 (^4J(C,P) = 2 Hz, *p*-P-Ph), 130.4 (*o*-C-Ph), 131.5 (^2J(C,P) = 9 Hz, *o*-P-Ph), 135.9 (^3J(C,P) = 5 Hz, *i*-C-Ph), 138.9 (^1J(C,P) = 105 Hz, *i*-P-Ph) 165.1 (^2J(C,P) = 12 Hz, = C). ^{31}P NMR (C_6D_6), δ (ppm): 16.4. MS (70 eV) *m/z*: 347 (M^+). Crystal data: crystal dimensions 0.5 mm × 0.4 mm × 0.3 mm, light yellow prisms, space group $P2_1/c$, monoclinic, $a = 9.484(2)$ Å, $b = 12.105(2)$ Å, $c = 16.523(3)$ Å, $\beta = 99.48(3)$ °, $V = 1871.0(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.233$ g cm^{-1}, 5433 reflections measured of which 2970 were independent of symmetry and 2385 were observed ($I > 2\sigma(I)$), $R1 = 0.039$, wR^2 (all data) = 0.107, 226 parameters.

$\{[Ph_3P{=}CHC(R)O]NbCl_3(TMS{-}C{\equiv}C{-}Ph)\}_2$ (4: R = Ph), (5: R = Me)

To a solution of $NbCl_3(TMS{-}C{\equiv}C{-}Ph){\cdot}(DME)$ (788 mg, 1.7 mmol/696 mg, 1.5 mmol) in CH_2Cl_2 $Ph_3P{=}CHC(O)Ph$ (784 mg, 1.7 mmol) or ($Ph_3P{=}CHC(O)Me$ (478 mg, 1.5 mmol) in CH_2Cl_2 was added. After stirring for two days the mixture was filtered, concentrated *in vacuo* and layered with hexane. Crystallization at −78 °C afforded a red–brown crystalline product (**4**: 769 mg, 60%; **5**: 374 mg, 36%).

Compound 4

M.p. 111 °C. Analysis: Calcd for $C_{74}H_{70}Cl_6Nb_2O_2P_2Si_2$ (1508.02)$\cdot CH_2Cl_2$: C, 56.55; H, 4.56; Cl, 17.80; Found: C, 56.72; H, 4.83; Cl, 16.46%. ^{31}P NMR ($CDCl_3$), δ (ppm): 22.3, (14.2 for the second isomer). IR (Nujol), $\tilde{\nu}$:1675 (alkyne, coordinated), 1528 (carbonyl, coordinated). Crystal data: crystal dimensions: 0.3 mm × 0.2 mm × 0.1 mm, red–brown prisms, space group $C2/c$, monoclinic, $a = 24.186(5)$ Å, $b = 15.031(3)$ Å, $c = 22.776(5)$ Å, $\beta = 94.66(3)$ °, $V = 8253(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.404$ g cm^{-1}, 5644 reflections measured of which 3032 were independent of symmetry and 897 were observed ($I > 2\sigma(I)$), $R1 = 0.086$, wR^2 (all data) = 0.218, 226 parameters.

Compound 5

M.p. 123 °C. Analysis: Calcd for $C_{64}H_{66}Cl_6Nb_2O_2P_2Si_2$ (1383.88)$\cdot CH_2Cl_2$: C, 53.15; H, 4.67; Cl, 19.31; Found: C, 53.15; H, 4.48; Cl, 19.03%. ^{31}P NMR ($CDCl_3$), δ (ppm): 20.3, 13.5 (for the two isomers). IR (Nujol), $\tilde{\nu}(cm^{-1})$:1667 (alkyne, coordinated), 1718 (alkyne, coordinated), 1526 (carbonyl, coordinated).

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