Reaction of 1,3-Diphospholyl Anions with Chlorotrimethylsilane: [1,5]-Sigmatropic Shifts of the Trimethylsilyl Group around the 1,3-Diphospholyl Ring

Michael L. Sierra, Nicole Maigrot, Claude Charrier, Louis Ricard, and François Mathey*

Laboratoire de Chimie du Phosphore et des Métaux de Transition, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France

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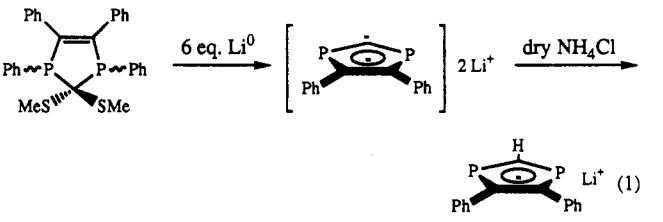
The protonation of the 4,5-diphenyl-1,3-diphospholyl anion, $[(PhC)_2P_2CH]^-$, in the presence of *N*-phenylmaleimide affords the [4 + 2] cycloadduct of the transient 4,5-diphenyl-2*H*-1,3-diphosphole, $[(PhC)_2P_2CH_2]$. The silylation by chlorotrimethylsilane of the $[P{\cdot}W(CO)_5]_2$ complex of this same anion at room temperature affords the corresponding complex of 1-(trimethylsilyl)-4,5-diphenyl-1*H*-1,3-diphosphole as the sole observable product. However, this 1,3-diphosphole complex is in equilibrium at room temperature with the corresponding 2-(trimethylsilyl)-4,5-diphenyl-2*H*-1,3-diphosphole via [1,5]-sigmatropic shifts of the silyl group. This 2*H*-1,3-diphosphole complex can be trapped as a [4 + 2] cycloadduct with dimethyl acetylenedicarboxylate. At −80 °C, these [1,5] shifts are frozen out and the silylation of the same complexed anion takes place exclusively at the carbons of the ring to give the 2-(trimethylsilyl)-4,5-diphenyl-2*H*-1,3-diphosphole and the 4-(trimethylsilyl)-4,5-diphenyl-4*H*-1,3-diphosphole complexes whose formation is demonstrated by trapping with dimethyl acetylenedicarboxylate.

Introduction

Together with phosphinines, phospholyl anions $[P_n(CR)_{5-n}]^-$ are the only known carbon–phosphorus heterocycles displaying any significant electronic delocalization.[1] At the moment, however, the organic chemistry of the recently discovered polyphospholyl anions remains largely unexplored. The only clear-cut results concern the protonation of $[P_3(C^tBu)_2]^-$ and $[P_2(C^tBu)_3]^-$, where $[P_3(C^tBu)_2]^-$ affords a cage compound via a complicated series of reactions[2] and a 1:1 mixture of $[P_2(C^tBu)_3]^-$ and $[P_3(C^tBu)_2]^-$ gives rise to a polyphosphorus [4 + 2] cycloadduct.[3] The only other available data on 1,3-diphospholyl species concern the synthesis of $[P_2(C^tBu)_3]^-$ in a 1:1 mixture with $[P_3(C^tBu)_2]^-$ by reductive cyclooligomerization of $^tBuC{\equiv}P$[4] along with the description of some of its π-complexes.[5] Recently, we have found a new synthetic route for the formation of 1,3-diphospholyl anions from 1,2-dihydro-1,2-diphosphetes.[6] These anions can now be readily prepared with various substitution schemes and are free of other organophosphorus-containing impurities. We report herein on their reaction with chlorotrimethylsilane and proton sources as well as the trapping of the resulting species.

Results and Discussion

For practical reasons, our study has been performed with the readily available 4,5-diphenyl-1,3-diphospholyl anion (1) made according to eq 1.[6] Anion 1 is the only resulting



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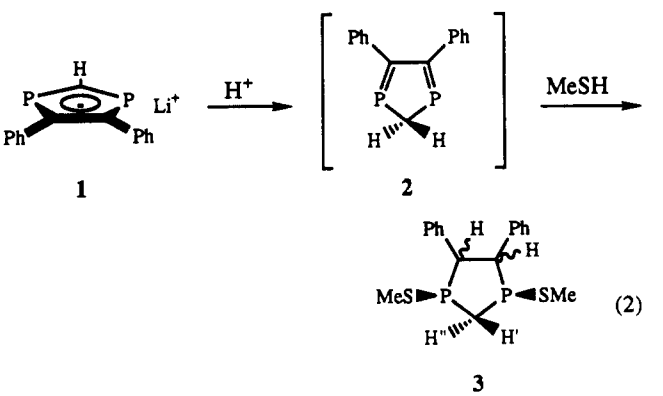
phosphorus-containing species of the reaction; however, it is accompanied by several organic byproducts including 2 equiv of methanethiol. Due to the presence of both MeSH in solution and solid NH_4Cl, the reaction of chlorotrimethylsilane with 1 led to the protonation product 2, which was instantaneously trapped by MeSH to afford the 1,3-diphospholane 3 (eq 2).



(2)

1 2 3

Only one isomer of 3 was obtained according to the ^{31}P NMR analysis of the reaction mixture. The two benzylic protons as well as the two phosphorus centers are equivalent, while the methylene protons are sharply nonequivalent with only one of these protons coupled to the two phosphorus atoms. Thus, the relative stereochemistry is as indicated in eq 2, however, the exact stereochemistry

(1) Selected references. $[PC_4R_4]^-$: Mathey, F. *New J. Chem.* **1987**, *11*, 585. Mathey, F. *Chem. Rev.* **1988**, *88*, 429. Douglas, T.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1367. $[P_3C_2R_2]^-$: Nixon, J. F. *Chem. Rev.* **1988**, *88*, 1327. $[P_5]^-$: Scherer, O. J.; Brück, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 59. Baudler, M.; Akpapoglou, S.; Ouzounis, D.; Wasgestian, F.; Meinigke, B.; Budzikiewicz, H.; Münster, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 280. Hamilton, T. P.; Schaefer, H. F., III *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 485.

(2) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1046.

(3) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1990**, 1307.

(4) Cowley, A. H.; Hall, S. W. *Polyhedron* **1989**, *8*, 849. Bartsch, R.; Nixon, J. F. *Polyhedron* **1989**, *8*, 2407.

(5) Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1146; Driess, M.; Hu, D.; Pritzkow, H.; Schaüfele, H.; Zenneck, U.; Regitz, M.; Rösch, W. *J. Organomet. Chem.* **1987**, *334*, C35. Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Organomet. Chem.* **1988**, *340*, C37. Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Organomet. Chem.* **1989**, *373*, C17. Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1990**, 472.

(6) Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 534.

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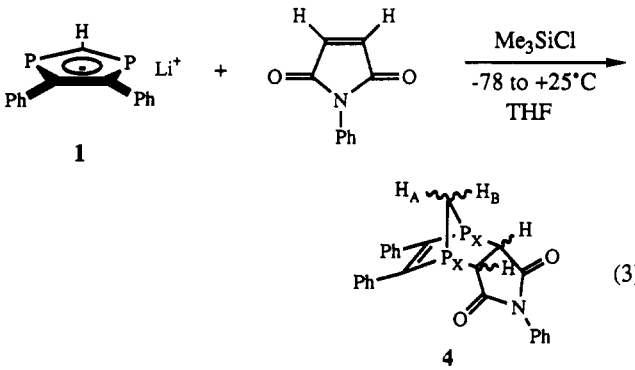
of the two phenyl groups is not known (i.e., both above or below the ring mean plane).

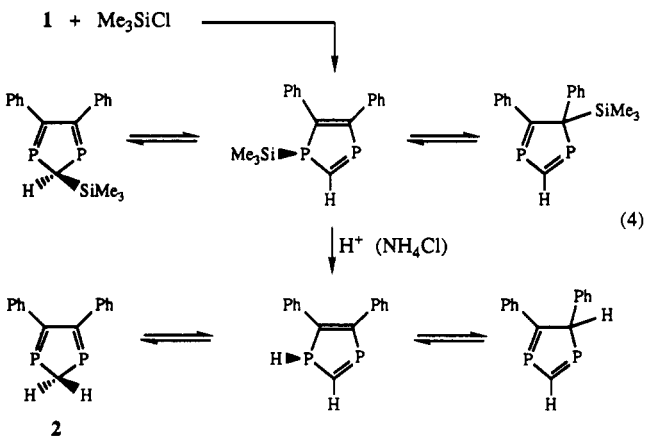
The intermediacy of the 1,3-diphosphole **2** was fully demonstrated via its trapping as a [4 + 2] cycloadduct with *N*-phenylmaleimide. The anion **1** was first freed from methanethiol by several thorough evaporations under vacuum. To the resulting product (**1** + NH_4Cl) was added *N*-phenylmaleimide in THF at −78 °C followed by the reaction with chlorotrimethylsilane, which was carried out between −78 °C and room temperature (eq 3). When the



(3)

addition of the reactants in eq 3 is reversed, so that the Me_3SiCl was added before the trapping agent, only oligomers of **2** were obtained. The structure of the cycloadduct **4** was easily established by its mass spectrum and ^{31}P NMR. The molecular peak of **4** appears at *m/e* 427–428 and the phosphorus centers are equivalent.

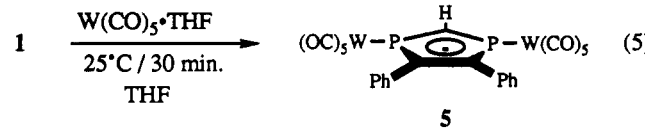
Since we know that both hydrogen[7] and the trimethylsilyl group[8] readily shift around the phospholyl ring even at low temperature, we rationalize the formation of **2** as in eq 4. Thus, the protonation would result from the



(4)

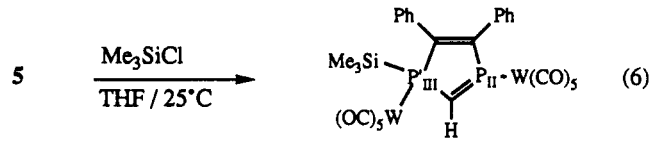
cleavage of the very labile P–Si bond by NH_4Cl with **2** as the most reactive among the three interconverting isomers of the 1,3-diphosphole, however, the initial silylation site is, of course, unknown.

In order to demonstrate this mechanism and to obtain more information on the site of the initial attack, it was necessary to slow down the [1,5] shifts and to strengthen the P–Si bond. From our previous work,[7,9] we knew that the complexation of the phosphorus atoms by tungsten pentacarbonyl was likely to inhibit the sigmatropic shifts. Accordingly, we allowed the anion **1**, freed from MeSH as described above, to react with $W(CO)_5$·THF. Simultaneous complexation of both phosphorus atoms was observed (eq 5). The ^{31}P resonance is shifted from δ +193 ppm for **1**



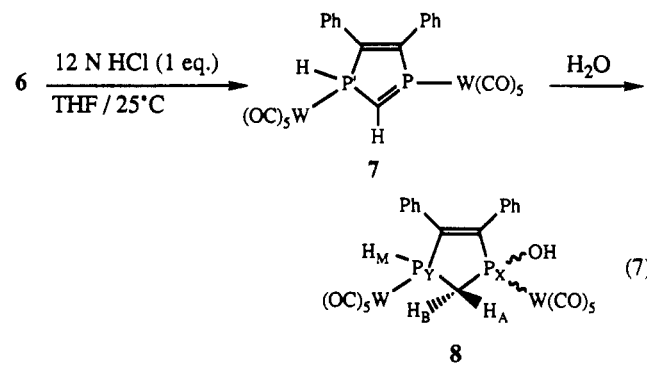
(5)

to δ +97 ppm for **5** (85% H_3PO_4 as external reference). A similar upfield shift has been previously observed upon the complexation of the 3,4-dimethylphospholyl anion by $W(CO)_5$.[8] The reaction of **5** with chlorotrimethylsilane at room temperature afforded the P–silyl derivative **6** as the sole observable product (eq 6). Compound **6** displays a



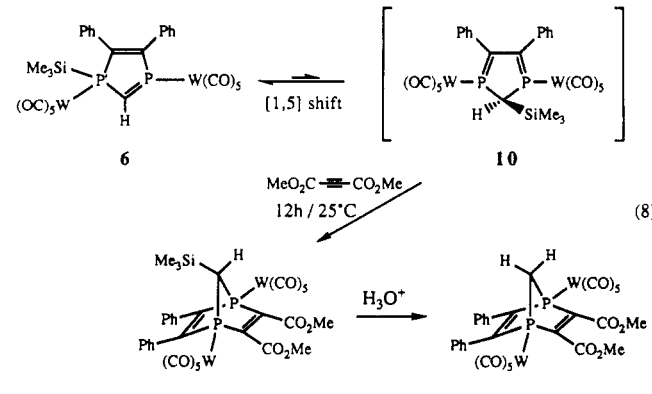
(6)

very characteristic ^{31}P NMR spectrum: δ +125.2 ppm, $^1J_{PW}$ = 302 Hz, $^2J_{PP'}$ = 24.4 Hz (P_{II}); δ −10.2 ppm, $^1J_{P'W}$ = 244 Hz (P'_{III}). Compound **6** also readily reacts with concentrated aqueous HCl to afford the corresponding P–H derivative **7** (eq 7), which also demonstrates a characteristic ^{31}P NMR of δ +132.8 ppm, $^2J_{PP'}$ = 30 Hz (P_{II}); δ −18.5 ppm, $^1J_{P'H}$ = 352 Hz (P'_{III}). Upon chromatography, compound **7** adds a molecule of water across the P=C double bond to afford **8** (eq 7), which was fully charac-



(7)

terized. At first glance, this series of results seems to establish that the silylation of **5** takes place at the phosphorus center; however, this is not the case. Indeed, the reaction of **6** with dimethyl acetylenedicarboxylate led exclusively to the formation of the [4 + 2] cycloadduct **9**, which indicates the existence of an equilibrium between **6** and **10** via a [1,5]-sigmatropic shift of the silyl group (eq 8). Compound **9** was characterized by ^{31}P NMR spec-



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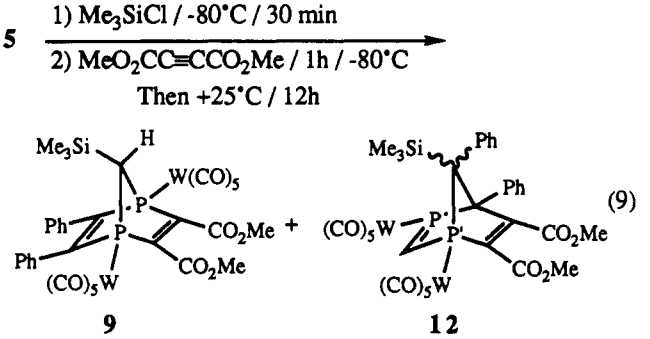
troscopy: δ 51.1 ppm, $^1J_{PW}$ = 239 Hz. The indicated

(7) Charrier, C.; Bonnard, H.; de Lauzon, G.; Mathey, F. *J. Am. Chem. Soc.* **1983**, *105*, 6871.
(8) Holand, S.; Mathey, F.; Fischer, J. *Polyhedron* **1986**, *5*, 1413.
(9) Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826.

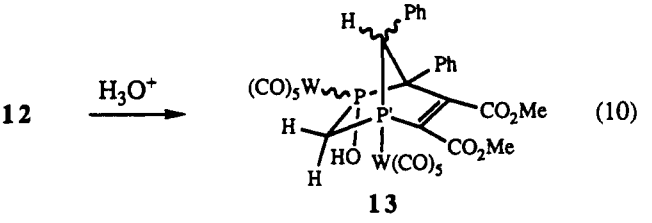
stereochemistry in **9** at the bridge carbon was not established but is logical since the cycloaddition very likely occurs on the less hindered face of the 1,3-diphosphole **10**. Upon chromatography over silica gel, the Si–C bond of **9** was hydrolyzed leading to the formation of **11**, which was fully characterized.

Although the equilibrium between **6** and **10** is shifted completely to the left, it is known from the literature[10] that the only phosphadienes that react with dienophiles to afford [4 + 2] cycloadducts have their phosphorus centers in the terminal positions. The driving force in these reactions can be attributed to the increase of the coordination number of phosphorus from 2 to 3. Similar observations have been made with the phosphadiene P·W(CO)$_5$ complexes.[11] Thus, **10** is predicted to be very reactive toward dimethyl acetylenedicarboxylate, whereas no reaction is expected for **6**. It is interesting to note that no cycloaddition takes place between **7** and dimethyl acetylenedicarboxylate, suggesting the absence of H-migration in this complex at room temperature.

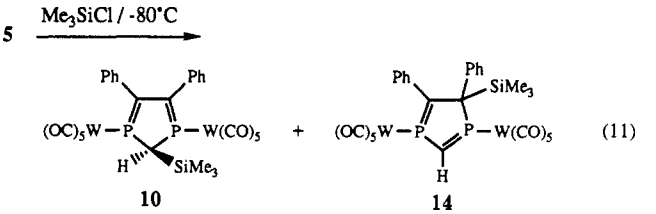
The existence of these [1,5] shifts gave no insight into the site of the initial silylation of **5**. It was thus necessary to repeat the same type of experiments at low temperature in order to inhibit these sigmatropic shifts. At −80 °C, the anion **5** was first allowed to react with chlorotrimethylsilane and then to this mixture was added dimethyl acetylenedicarboxylate. The [4 + 2] cycloadducts **9** and **12** were thus obtained in ca. 40:60 ratio (eq 9). Compound



12 was characterized by ^{31}P NMR spectroscopy (δ 135.1 ppm, $^2J_{PP'}$ = 24 Hz (P_{II}); δ 43.1 ppm (P'_{III})); however, we have no information on the stereochemistry at the bridge carbon. Upon chromatography, the Si–C bond was hydrolyzed and one molecule of water added across the P=C double bond to give **13**, which was fully characterized (eq 10).



We have checked that the ratio **9**:**12** does not change with reaction time at −80 °C. Thus, the trapping of the 1,3-diphosphole with dimethyl acetylenedicarboxylate is probably complete within 1 h at −80 °C. As a consequence, our results mean that the silylation of **5** at −80 °C affords ca. a 40:60 mixture of 1,3-diphospholes **10** and **14** (eq 11).



Preliminary theoretical calculations have been carried out on the parent 1,3-diphospholyl anion.[12] The net charges at the various atoms of the ring are calculated to be P, +0.11; C_2, −0.48; and C_4 or C_5, −0.32. These data fit well our own results demonstrating the silylation of **5** at the carbon centers of the ring.

Experimental Section

General Data. All reactions were performed under an argon atmosphere. Solvents were purified and dried by standard techniques. All glassware used in the synthetic work was oven dried. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 SY operating at 200.13 and 50.32 MHz, respectively, while ^{31}P spectra were recorded on a Bruker WP 80 SY operating at 32.44 MHz. All chemical shifts are reported in parts per million downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct-inlet method. Elemental analyses were performed by Service de microanalyse, Gif-sur-Yvette, France. These compounds are oxygen and water sensitive so that their oxides are sometimes observed in the analyses.

Synthesis of 1. The 1,3-diphosphacyclopentadienyl anion was prepared as described by Mathey[6] with only slight modifications to the procedure. The formation of the dianion is complete within 3 h and then 5 equiv of anhydrous NH_4Cl is added at 0 °C to afford **1** cleanly with immediate protonation of the dianion. **1** is then used directly unless otherwise stated. ^{31}P NMR (THF) δ 193.

Synthesis of 3. To a solution of **1** (1 g, 4 mmol) in 25 mL of THF at −78 °C was added 507 μL of Me_3SiCl (4 mmol). After stirring for 1 h at −78 °C, the reaction mixture was slowly warmed to room temperature and stirred an additional 12 h. After evaporation of THF, the mixture was chromatographed over silica gel (60 mesh) with hexane/toluene (50/50). Compound **3** was isolated as a viscous yellow-orange oil. Yield 44%. Mass spectrum: *m/e* 350 (M^+, 40%), 170 (M − $(PhCH)_2$, 100%). Anal. Calcd for $C_{17}H_{20}P_2S_2 \cdot {}^1/_2C_7H_8$: C, 61.85 (62.12); H, 5.84 (6.06). ^{31}P NMR ($CDCl_3$) δ 65.7. ^{1}H NMR ($CDCl_3$): δ 7.50–7.00 (m, 10 H, phenyl), 4.28 (m, $|^2J_{HP} + {}^3J_{HP}|$ = 9 Hz, 2 H, benzylic), 2.79 (dt, $^2J_{H'H''}$ = 15.4 Hz, $^2J_{H'P}$ = 31 Hz, 1 H, $P_2CH'H''$), 2.30 (d, $^3J_{HP}$ = 12.7 Hz, 6 H, $PSCH_3$), 2.29 (d, $^2J_{H'H''}$ = 15.4 Hz, $^2J_{H''P}$ = 0 Hz, 1 H, $P_2CH'H''$) [toluene: δ 7.2 (m, phenyl), 2.3 (s, CH_3)]. ^{13}C NMR ($CDCl_3$) δ 138.0 (C_{ipso}), 129.2 (C_{ortho}), 128.6 (C_{meta}), 126.5 (C_{para}), 57.4 (d, $^1J_{CP}$ = 20 Hz, $C_{benzylic}$), 27.5 (t, $^1J_{CP}$ = 35 Hz, CH_2), 16.8 (d, $^2J_{CP}$ = 27 Hz, SCH_3) [toluene: δ 137.8 (C_{ipso}), 129.1 (C_{ortho}), 128.5 (C_{meta}), 125.3 (C_{para}), 22.7 (CH_3)].

Synthesis of 4. A solution of **1** (1 g, 4 mmol) in 25 mL of THF was evaporated to dryness several times to remove all free MeSH. **1** was then dissolved in 20 mL of THF and cooled to −78 °C and *N*-phenylmaleimide (1.04 g, 6 mmol) was added followed immediately by 507 μL of Me_3SiCl (4 mmol). After stirring for 15 min at −78 °C, the reaction mixture was slowly warmed to room temperature and stirred an additional 12 h. After evaporation of THF, the mixture was chromatographed over silica gel (60 mesh) with toluene followed by toluene/ethyl acetate (90/10). Compound **4** was isolated as a yellow solid. Yield 35%. Mp 84–85 °C. Anal. Calcd for monooxide $C_{25}H_{19}NO_3P_2$: C, 67.25 (67.72); H, 4.92 (4.33). ^{31}P NMR ($CDCl_3$) δ 70.8. ^{1}H NMR ($CDCl_3$): δ 7.30–7.10 (m, 15 H, phenyl), 3.67 (pseudotriplet (pt), 2 H, methyne), 1.87 (part A of an ABX_2 system, $^2J(H_AH_B)$ = 15 Hz, $^2J(H_AP_X)$ = 12 Hz, 1 H, $P_2CH_AH_B$), 1.13 (part B of an ABX_2

(10) Appel, R. In *Multiple Bonds and Low Coordination in Phorphorus Chemistry*; Regitz, H., Scherer, O. J., Eds.; Georg Thiene Verlag: Stuttgart, 1990; pp 157–219.
(11) Tran Huy, N. H.; Mathey, F. *Tetrahedron Lett.* **1988**, *29*, 3077. Maigrot, N.; Charrier, C.; Ricard, L.; Mathey, F. *Polyhedron* **1990**, *9*, 1363. Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *J. Chem. Soc., Dalton Trans.*, in press.

(12) Nixon, J. F.; Sillett, G. J. D., personal communication. Sillett, G. J. D. Ph.D. Thesis, University of Sussex, G.B., 1991.

system, $^2J(H_AH_B)$ = 15 Hz, $^2J(H_BP_X)$ = 12.5 Hz, 1 H, $P_2CH_AH_B$). ^{13}C NMR ($CDCl_3$) δ 175.0 (pt, CO), 137.2 (pt, C:), 134.8-125.6 (phenyl), 25.6 (t, $^1J_{CP}$ = 20 Hz, P_2CH_2), 47.5 (pt, CH).

Synthesis of 5. A solution of 1 (1 g, 4 mmol) in 25 mL of THF was evaporated to dryness several times to remove all free MeSH. 1 was then dissolved in 20 mL of THF and added to a solution of $W(CO)_5$·THF in THF, prepared by the photolysis of $W(CO)_6$ (4.2 g, 12 mmol) in the presence of 300 mL of THF. After stirring the reaction mixture for 30 min at room temperature, the solvent was concentrated in vacuo to ca. 25 mL to afford a solution of 5 (4 mmol), which was used without further purification. ^{31}P NMR (THF) δ 97 ($^1J_{WP}$ = 200 Hz).

Synthesis of 6-8: A solution of 5 (4 mmol) in 25 mL of THF was stirred with 762 μL of Me_3SiCl (6 mmol) for 15 min at room temperature, thus yielding 6. Directly to 6 was added 333 μL of 12 N HCl (4 mmol) to afford 7. After evaporation of THF, the mixture was chromatographed over silica gel (60 mesh) with toluene/ethyl acetate (50/50), which led to the hydrolysis of the P=C double bond and 8 was isolated as a viscous red-orange semisolid. Yield 25%. Anal. Calcd for $C_{25}H_{14}O_{11}P_2W_2 \cdot C_4H_8O_2$: C, 34.26 (34.55); H, 2.28 (2.20). 6: ^{31}P NMR (THF) δ 125.2 (P_{II}), -10.2 (P'_{III}) ($^2J_{PP'}$ = 24.4 Hz, $^1J_{WP}$ = 302 Hz, $^1J_{WP'}$ = 244 Hz). 7: ^{31}P NMR (THF) δ 132.8 (P_{II}), -18.5 (P'_{III}) ($^2J_{PP'}$ = 30 Hz, $^1J_{HP'}$ = 352 Hz). 8: ^{31}P NMR ($CDCl_3$) δ 136.4 (P_X), -29.2 (P_Y) ($^2J(P_XP_Y)$ = 19.5 Hz, $^1J(H_MP_Y)$ = 330 Hz, $^1J(WP_X)$ = 273 Hz, $^1J(WP_Y)$ = 244 Hz). ^1H NMR ($CDCl_3$) δ 7.40-6.80 (m, 10 H, phenyl), 6.38 (part M of an ABMXY system, $^1J(H_MP_Y)$ = 330 Hz, $^3J(H_BH_M)$ = 8.0 Hz, $^3J(H_AH_M)$ = 6.0 Hz, $^3J(H_MP_X)$ = 3.8 Hz, H_M), 3.34 (part A of an ABMXY system, $^2J(H_AH_B)$ = 15.0 Hz, $^3J(H_AH_M)$ = 6.0 Hz, $^2J(H_AP_X)$ = 6.0 Hz, $^2J(H_AP_Y)$ = 6.0 Hz, 1 H, H_A), 2.95 (part B of an ABMXY system, $^2J(H_AH_B)$ = 15.0 Hz, $^3J(H_BH_M)$ = 8.0 Hz, $^2J(H_BP_X)$ = 11.0 Hz, $^2J(H_BP_Y)$ = 1.2 Hz, 1 H, H_B) [ethyl acetate: δ 4.07 (q, OCH_2), 2.01 (s, CH_3CO), 1.2 (t, CH_2CH_3)]. ^{13}C NMR (acetone-d_6) δ 199.8 (pt, CO_{ax}), 196.3 (pt, CO_{eq}), 136.5-129.2 (phenyl), 153.9 (dd, $^1J(CP_X)$ = 37 Hz, $^2J(CP_Y)$ = 11 Hz, C:), 142.9 (dd, $^1J(CP_Y)$ = 35 Hz, $^2J(CP_X)$ = 16 Hz, C:), 34.4 (dd, $^1J(CP_X)$ and $^1J(CP_Y)$ = 18 and 15 Hz, CH_2).

Synthesis of 9 and 11. A solution of 5 (4 mmol) in 25 mL of THF was stirred with 762 μL of Me_3SiCl (6 mmol) for 15 min at room temperature, thus yielding 6. Directly to 6 was added 568 μL of dimethyl acetylenecarboxylate (4 mmol) and the reaction allowed to stir for an additional 12 h at room temperature. After evaporation of THF, 9 was identified by its ^{31}P NMR, but upon chromatography of the mixture over silica gel (60 mesh) with toluene/ethyl acetate (50/50) hydrolysis of the Si-C bond was observed and 11 was isolated as a dark orange solid. Yield 45%. Mp, decomposes 144 °C. Anal. Calcd for $C_{31}H_{18}O_{14}P_2W_2$: C, 35.73 (35.66); H, 2.33 (1.74). 9: ^{31}P NMR (THF) δ 51.1 ($^1J_{WP}$ = 239 Hz). 11: ^{31}P NMR ($CDCl_3$) δ 50.2 ($^1J_{WP}$ = 244 Hz). ^1H NMR ($CDCl_3$) δ 7.30-7.10 (m, 10 H, phenyl), 3.99 (s, 6 H, OMe), 3.00 (m, 2 H, P_2CH_2). ^{13}C NMR ($CDCl_3$) δ 196.6 (pt, CO_{ax}), 194.2 (d, CO_{eq}), 164.4 (pt, CO_2), 157.7 (pt, O_2CC:), 156.6 (pt, PhC:), 133.8 (pt, C_{ipso}), 129.1-128.2 (C_{ortho}, C_{meta}, C_{para}), 55.8 (t, $^1J_{CP}$ = 20 Hz, P_2CH_2), 53.6 (s, OMe).

Synthesis of 12 and 13. A solution of 5 (4 mmol) in 25 mL of THF at -78 °C was stirred with 762 μL of Me_3SiCl (6 mmol) for 5 min; then 568 μL of dimethyl acetylenedicarboxylate (4 mmol) was added. After it was stirred for 1 h at -78 °C, the reaction mixture was slowly warmed to room temperature and stirred for an additional 12 h. The ^{31}P NMR revealed that a mixture of 9 and 12 was obtained in a ratio of 40:60, but upon chromatography of the mixture over silica gel (60 mesh) with toluene and then toluene/ethyl acetate (90/10), hydrolysis of the Si-C bond and P=C double bond in 12 was observed and compounds 11 (20%) and 13 (26%) were isolated. Compound 13: mp, decomposes 74-75 °C. Anal. Calcd for $C_{31}H_{20}O_{15}P_2W_2 \cdot {}^1/_2C_7H_8$: C, 37.18 (37.39); H, 2.08 (2.19). 12: ^{31}P NMR (THF) δ 135.1 (P), 43.1 (P') ($^2J_{PP'}$ = 24 Hz). 13: ^{31}P NMR ($CDCl_3$) δ 138.9 (P), 43.3 (P') ($^2J_{PP'}$ = 19.6 Hz, $^1J_{WP'}$ = 288 Hz, $^1J_{WP}$ = 254 Hz). ^1H NMR ($CDCl_3$) δ 7.31-7.24 (m, 10 H, phenyl), 4.05 (s, 3 H, OMe), 3.93 (s, 3 H, OMe), 3.75 (m, 2 H, P_2CH_2), 3.35 (m, 1 H benzylic). ^{13}C NMR ($CDCl_3$) δ 197.7 (m, CO_{ax}), 195.1 (m, CO_{eq}), 165.8 (d, $^3J_{CP'}$ = 2.7 Hz, CO_2), 163.4 (d, $^2J_{CP'}$ = 18.6 Hz, CO_2), 153.4 (dd, J_{CP} and $J_{CP'}$ = 36.8 and 14.8 Hz, C:), 146.9 (dd, J_{CP} and $J_{CP'}$ = 32.5 and 12 Hz, C:), 145.8-125.2 (phenyl), 53.5 (s, OMe), 52.9 (s, OMe), 52.9 (m, PCPh, P'CHPh), 38.3 (t, $^1J_{CP'} \cong {}^1J_{CP} \cong$ 14.3 Hz, P_2CH_2).

Synthesis of the Prototype of the Trans Diacyl Complex of Platinum by Intramolecular CO Transfer in an Alkyl α-Ketoacyl Complex. Crystal Structures of *trans*-Pt(Et)(COCOPh)(PPh_3)$_2$ and *trans*-Pt(COEt)(COPh)(PPh_3)$_2$

Jwu-Ting Chen,* Tsang-Miao Huang, Ming-Chu Cheng, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

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The reaction of *trans*-[Pt(COCOPh)(THF)(PPh_3)$_2$](BF_4) (1) with $LiBHEt_3$ gives *trans*-Pt(H)(COCOPh)(PPh_3)$_2$ (2) and *trans*-Pt(Et)(COCOPh)(PPh_3)$_2$ (3), both in poor yield. In contrast, complex 3 may be formed in an excellent 90% yield, by using Et_2Zn as the alkylating agent. Unlike other trans (α-ketoacyl)platinum complexes in which the two α-ketoacyl carbonyls are near planar, 3 comprises "perpendicular" α-ketoacyl carbonyls whose torsional angle O3-C3-C4-O4 is 114.7 (9)°. In the presence of PPh_3 or in the coordinating solvent such as THF, 3 can be stable at ambient temperature. In noncoordinating solvent such as CH_2Cl_2 or $CHCl_3$, 3 undergoes spontaneous intramolecular CO transfer to form a prototype of trans diacyl complex, *trans*-Pt(COEt)(COPh)(PPh_3)$_2$ (4). The two acyl carbonyls in 4 are in the s-cis configuration which is distinct from the s-trans feature of the acyl carbonyls in its cis isomers.

Introduction

We have previously reported the synthesis of the novel cis diacylplatinum complexes in prototype, *cis*-Pt(COR)(COR')(PPh_3)$_2$ (wherein, R, R' = alkyl or aryl) by the reactions of cis acyl carbonyl complex of platinum with organolithium.[1] Its reaction mechanism, unlike the analogous reactions using alkoxide or amine as the nucleophile, presumably first undergoes nucleophilic attack of the carbon-centered nucleophile at the Pt(II) center

(1) Chen, J.-T.; Huang, T.-M.; Cheng, M.-C.; Wang, Y. *Organometallics* **1990**, *9*, 539.

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