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Generating Phosphinidene−*N*-Methylimidazole Adducts under Mild Conditions

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The nucleophilic attack of *N*-methylimidazole at the bridge phosphorus of a 7-phosphanorbornadiene pentacarbonylmolybdenum complex induces the collapse of the bridge. According to DFT calculations, the resulting zwitterion displays a very long and weak P−Mo bond. The excess of *N*-methylimidazole thus appears to be able to displace the phosphinidene from its molybdenum complex. The final result is a phosphinidene−*N*-methylimidazole adduct whose structure has also been computed. When applied to the phenyl derivative at 40 °C in toluene, this reaction effectively generates the [PhP] adduct, which decomposes to give essentially Ph_4P_4 and Ph_5P_5. At 80 °C, $PhPH_2$ is also produced. In the presence of CCl_4 the phosphinidene adduct inserts into the C−Cl bond to give $PhP(Cl)CCl_3$.

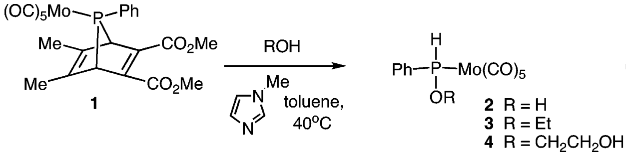
Introduction

The chemistry of phosphinidenes is presently poorly developed,[1] in part as a result of the lack of versatile methods for their generation under mild conditions. The two main methods, i.e., the thermal depolymerization of cyclopolyphosphines at high temperature and the reduction of dihalophosphines by electropositive metals, are, indeed, hardly compatible with any reactive functional substituent and generate a lot of products other than the desired six-electron monomeric species. In addition, most of the phosphinidenes have a triplet ground state[2] and their chemistry appears to be rather erratic. In fact, presently, only two phosphinidenes have been generated and convincingly characterized by spectral methods and trapping reactions, i.e., [^{t}Bu$_2$P−P][3] and [Mes−P].[4] In both cases, their chemistry is characteristic of a singlet state. In this report, we present a simple access to singlet *N*-methylimidazole adducts of these species that could significantly extend the scope of phosphinidene chemistry.

Results and Discussion

It has been recently shown that the reaction of 7-phosphanorbornadiene complexes with mild nucleophiles (stabilized phosphorus ylides, malonate anions, fluoride ions) induces the collapse of the phosphorus bridge under mild conditions.[5] This observation led us to wonder what would happen if we used as the nucleophile a base devoid of reactive bonds. In fact, an example already exists where the nucleophile is tributylphosphine.[6] The result is a zwitterionic adduct between the phosphinidene bridge and tributylphosphine whose chemistry is similar to that of a classical phosphorus ylide.[7] Among the possible nucleophiles, *N*-methylimidazole appeared as a logical choice since it is both a good nucleophile and a good ligand of group VI metals.[8] We thus decided to study the reaction of a representative 7-phosphanorbornadiene complex such as **1** with this sp^2-N base.

For convenience, we start with the case where water or an alcohol is present as a co-reagent in the reactive medium. In this case, not surprisingly, the product of the reaction corresponds to the insertion of the phosphinidene bridge into the O−H bond.[9] The only difference with the case where no *N*-methylimidazole is present is that the collapse of the bridge and the insertion reaction take place at lower temperature and proceed in higher yield with the base (eq 1).



(1)

With water, the reaction goes to completion in ca. 30 h at 40 °C. With ethanol, the reaction is complete in 6 h and the product

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(1) Reviews: Schmidt, U. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 523. Mathey F. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, 1990; pp 33−38. Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998; pp 14−18. For more recent data, see: Shah, S.; Simpson, M. C.; Smith, R. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2001**, *123*, 6925.

(2) Nguyen, M. T.; Van Keer, A.; Vanquickenborne, L. G. *J. Org. Chem.* **1996**, *61*, 7077.

(3) Fritz, G.; Vaahs, T.; Fleischer, H.; Matern, E. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 315. Fritz, G.; Vaahs, T.; Fleischer, H.; Matern, E. *Z. Anorg. Allg. Chem.* **1989**, *570*, 54.

(4) Li, X.; Lei, D.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 8526. Li, X.; Weissman, S. I.; Lin, T.-S.; Gaspar, P. P.; Cowley, A. H.; Smirnov, A. I. *J. Am. Chem. Soc.* **1994**, *116*, 7899. Bucher, G.; Borst, M. L. G.; Ehlers, A. W.; Lammertsma, K.; Ceola, S.; Huber, M.; Grote D.; Sander, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 3289.

(5) Hoffmann, N.; Wismach, C.; Jones, P. G.; Streubel, R.; Tran Huy, N. H.; Mathey, F. *Chem. Commun.* **2002**, 454. Tran Huy, N. H.; Compain, C.; Ricard, L.; Mathey, F. *J. Organomet. Chem.* **2002**, *650*, 57. Compain, C.; Tran Huy, N. H.; Mathey, F. *Heteroat. Chem.* **2004**, *15*, 258. Compain, C.; Mathey, F. *Z. Anorg. Allg. Chem.* **2006**, *632*, 421.

(6) Le Floch, P.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1990**, *112*, 2407.

(7) Similar transient adducts are formed with electron-rich nitriles: Streubel, R. *Top. Curr. Chem.* **2003**, *223*, 91.

(8) Ardizzoia, G. A.; Brenna, S.; LaMonica, G.; Maspero, A.; Masciocchi, N. *J. Organomet. Chem.* **2002**, *649*, 173.

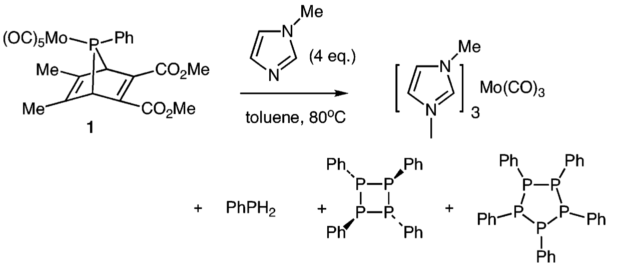
(9) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488.

10.1021/om060460m CCC: $33.50

is isolated in 84% yield. The same conditions are used for the reaction with glycol. The product is isolated in 49% yield. The ^{13}C NMR spectrum of **4** shows two OCH_2 groups at 62.18 (J_{C-P} = 6.3 Hz) and 73.94 (J_{C-P} = 14.6 Hz) in $CDCl_3$. For comparison, the reaction of ethanol with **1** alone goes to completion in 16 h at 110 °C and **3** is isolated in 27% yield.

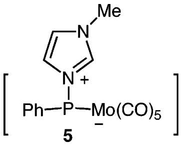
The reaction of **1** with *N*-methylimidazole was also run in the presence of diphenylacetylene and 2,3-dimethylbutadiene. The formation of the expected phosphirene or vinylphosphirane complexes was not observed. Since [PhP−Mo(CO)$_5$] is known to react with these unsaturated compounds to give three-membered rings, its intermediacy is ruled out.

In the absence of protic reagent, the reaction of *N*-methylimidazole proceeds in a different way. It is typically carried out at 80 °C in toluene with 4 equiv of heterocyclic base. The three main products of the reaction are phenylphosphine, which was easily identified by ^{31}P NMR (δ^{31}P −125, triplet, $^1J_{H-P}$ = 195.5 Hz), tetraphenylcyclotetraphosphine, which was recovered in 35% yield by chromatography and identified by ^{31}P NMR (δ^{31}P −55 in CD_2Cl_2, singlet)[10] and mass spectrometry (molecular peak at 433), and pentaphenylcyclopentaphosphine, which was recovered in 10% yield by chromatography and characterized by ^{31}P NMR (δ^{31}P −5 in CD_2Cl_2, multiplet)[11] and mass spectrometry (molecular peak at 541). Molybdenum was recovered as its already described tris-imidazole complex[8] that precipitates from the toluene solution (eq 2).



When run at 40 °C, the reaction does not produce any primary phosphine, but exclusively yields the oligomers.

By analogy with the case of tributylphosphine,[6] it was tempting to interpret these results as follows. The nitrogen base would attack the bridge of **1** near room temperature to produce the zwitterionic adduct **5**. In **5**, phosphorus is not electrophilic as in [PhP−Mo(CO)$_5$] but nucleophilic. We thus expect a fast protonation by water and alcohols but no reaction with alkynes or conjugated dienes. It must be noted here that a terminal phosphinidene Fe(CO)$_4$ complex has been stabilized by chelation with a nitrogen base.[12]



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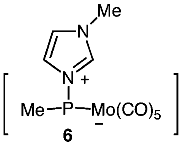

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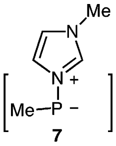

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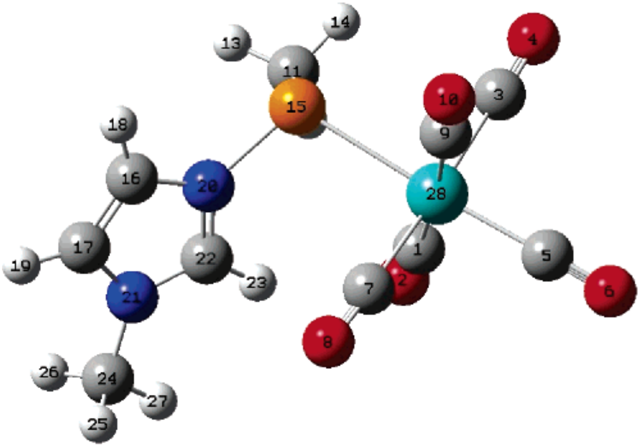
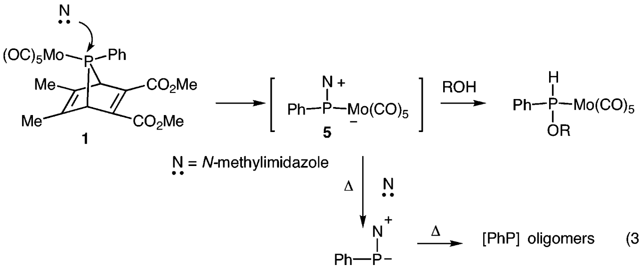


Figure 1. Computed structure of complex **6**. Main bond lengths (Å) and angles (deg): P15−N20 1.897, P15−C11 1.878, P15−Mo28 2.642; C11−P15−N20 94.94, C11−P15−Mo28 108.00, N20−P15−Mo28 106.61.

To confirm this hypothesis, we decided to perform DFT calculations[13] on **6** using the B3LYP functional with the 6-31G(d) basis sets for all atoms except Mo (lanl2dz). The results were quite interesting. The computed structure of **6** is shown in Figure 1. This structure corresponds to a shallow but genuine local minimum (no negative frequency). Phosphorus is pyramidal (∑angles at P = 309.5°). The only unexpected result is the very long P−Mo bond at 2.642 Å. Such bond lengths typically lie between 2.37 and 2.53 Å.[14] Thus, it becomes highly likely that *N*-methylimidazole is able to displace the phosphinidene from its labile molybdenum complex. This observation supports the proposed mechanism that is summarized in eq 3.



(3)

At this point, as noted by several referees, the question becomes whether the decomplexation reaction initially yields the free phosphinidene or a zwitterionic adduct with the base. We thus decided to compute the structure of the [MeP]-*N*-methylimidazole adduct **7** at the B3LYP 6-311+G(d,p) level. We found a genuine minimum (no negative frequency), whose structure is shown in Figure 2. The most striking characteristic of this structure is the strict coplanarity of the P−Me bond and imidazole ring, probably reflecting a stabilizing interaction between the π lone pair at P and the imidazole π system. The frontier orbitals of **7** are shown in Figure 3. The HOMO is essentially localized at P and corresponds to the π lone pair.

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(10) Breen, T. L.; Stephan, D. W. *Organometallics* **1997**, *16*, 365.

(11) Fermin, M. C.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 12645.

(12) Cowley, A. H.; Geerts, R. L.; Nunn, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 9, 6523.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2003.

(14) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Le Van, D.; Krebs, B.; Läge, M. *Organometallics* **2002**, *21*, 2921.

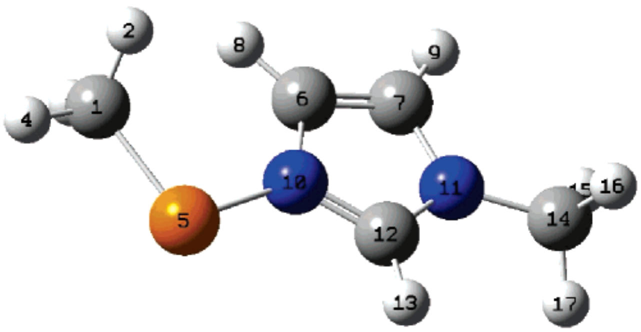
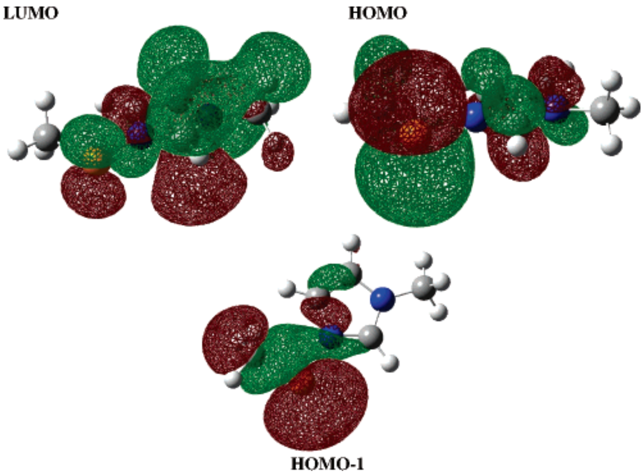


Figure 2. Computed structure of adduct **7**. Main bond lengths (Å) and angles (deg): P15−N20 C1−P5 1.869, P5−N10 1.829, N10−C6 1.392, C6−C7 1.366, C7−N11 1.372, N11−C12 1.361, C12−N10 1.342; C1−P5−N10 97.09, P5−N10−C12 124.51, C6−N10−C12 106.29.


LUMO

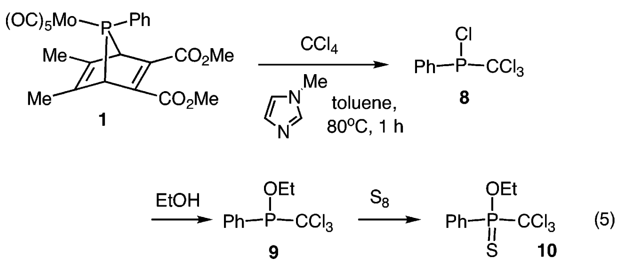
HOMO

HOMO-1

Figure 3. Kohn−Sham orbitals of adduct **7**.

The HOMO−1 corresponds to the in-plane σ lone pair at P. The LUMO is mainly localized on the imidazole ring. These observations completely fit a zwitterionic formulation with a nucleophilic phosphorus.

We were eager to find a reaction that would be characteristic of these imidazole adducts. It is known that tetrachloromethane reacts with terminal phosphinidene complexes to give the corresponding dichlorophosphine complexes,[15] whereas it reacts with cyclopolyphosphines to give the corresponding chlorotrichloromethylphosphines via a stepwise depolymerization reaction at high temperature.[16] Our system reacts with CCl_4 in toluene at 80 °C to give chlorotrichloromethylphenylphosphine (eq 5).



The reaction is complete in less than 1 h, and **8** is the sole P-containing product according to the monitoring of the reaction mixture by ^{31}P NMR. These conditions are substantially milder than those used for the reaction of Ph_4P_4 (reflux in pure CCl_4 for 20 h), thus highlighting the enhanced nucleophilicity of our adducts. The chlorophosphine **8** was detected by its ^{31}P resonance at 96.4 ppm in toluene and reacted with ethanol and sulfur for full characterization.

The net effect of the complexation of phosphinidenes by *N*-methylimidazole is to stabilize the singlet state and to enhance the nucleophilicity of phosphorus. Since the proposed access to these adducts is both simple and versatile, we expect the development of interesting synthetic applications around these new P(I) species.

Experimental Section

Reactions were performed under nitrogen using oven-dried glassware. Dry tetrahydrofuran was obtained by distillation from Na/benzophenone. Silica gel (70−230 mesh) was used for chromatographic separation. Nuclear magnetic resonance spectra were obtained on a Bruker Avance 300 and Varian Inova spectrometer operating at 300.13 MHz for ^{1}H, 75.45 MHz for ^{13}C, and 121.496 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from external TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Mass spectra were obtained on VG 7070 and Hewlett-Packard 5989A GC/MS spectrometers. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ.

(Phenylphosphinous acid)pentacarbonylmolybdenum (2). The (7-phosphanobornadiene)pentacarbonylmolybdenum complex **1** (0.15 g, 0.27 mmol), 1-methylimidazole (0.09 mL, 1.08 mmol), and water (0.005 mL, 0.27 mmol) were heated at 40 °C in toluene (1.5 mL) for 30 h. After evaporation, the residue was purified by column chromatography on silica gel (2:1 hexane−dichloromethane) to afford complex **2** (0.087 g, 89% yield): R_f 0.3 (CH_2Cl_2); ^{31}P NMR ($CDCl_3$) δ 107.1 (P−H, $^1J_{PH} = 343.7$ Hz $^3J_{PH} = 11.9$ Hz); ^{1}H NMR ($CDCl_3$) δ 1.69 (OH), 7.47−7.64 (m, 5H, Ph), 7.90 (d, $^1J_{P-H} = 341.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 129.21−138.30 (m, C ortho, meta, para), 204.80 (d, $^2J_{C-P} = 10.1$ Hz, CO cis), 209.35 (d, $^2J_{C-P} = 26.4$ Hz, CO trans); MS (FAB, ^{98}Mo) *m/z* 364 (M^+, 61%), 336 (M − CO, 20%), 308 (M − 2CO, 27%), 280 (M − 3CO, 22%), 252 (M − 4CO, 10%), 224 (M − 5CO, 25%). Anal. Calcd for $C_{11}H_7MoO_6P$: C, 36.49; H, 1.95. Found: C, 36.85; H, 2.33.

(*O*-Ethyl phenylphosphinite)pentacarbonylmolybdenum (3). The (7-phosphanobornadiene)pentacarbonylmolybdenum complex **1** (1 g, 1.77 mmol), 1-methylimidazole (0.57 mL, 7.08 mmol), and ethanol (0.1 mL, 1.77 mmol) were heated at 40 °C in toluene (10 mL) for 6 h. After vacuum distillation, the residue was chromatographed on silica gel with petroleum ether−ethyl ether (20:1) as the eluent to yield 0.58 g (84%) of a blue solid: R_f 0.5 (petroleum ether); ^{31}P NMR ($CDCl_3$) δ 123.3 (P−H, $^1J_{PH} = 325.9$ Hz); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, $^3J_{H-H} = 7.0$ Hz, CH_3), 3.54−3.77 (m, CH_2), 7.46−7.62 (m, 5H, Ph), 7.57 (d, $^1J_{P-H} = 327.7$ Hz); ^{13}C NMR ($CDCl_3$) δ 16.25 (d, $^3J_{C-P} = 5.7$ Hz, CH_3), 68.96 (d, $^2J_{C-P} = 14.6$ Hz, CH_2), 125.50−136.26 (m, C ortho, meta, para), 204.94 (d, $^2J_{C-P} = 10.1$ Hz, CO cis), 209.91 (d, $^2J_{C-P} = 27.2$ Hz, CO trans); MS (FAB, ^{98}Mo) *m/z* 392 (M^+, 53%), 364 (M − CO, 38%), 336 (M − 2CO, 21%), 308 (M − 3CO, 36%), 280 (M − 4CO, 6%), 252 (M − 5CO, 22%). Anal. Calcd for $C_{13}H_{11}MoO_6P$: C, 40.02; H, 2.84. Found: C, 40.07; H, 2.92.

(*O*-2-Hydroxyethyl phenylphosphinite)pentacarbonylmolybdenum (4). The (7-phosphanobornadiene)pentacarbonylmolybdenum complex **1** (1 g, 1.77 mmol), 1-methylimidazole (0.57 mL, 7.08 mmol), and ethylene glycol (0.1 mL, 1.77 mmol) were heated at 40 °C in toluene (10 mL) for 6 h. After evaporation of the solvent, the residue was purified by chromatography on silica gel. Elution with petroleum ether−ethyl ether (1:1) gave 0.35 g of complex **4**, yield 49%: R_f 0.4 (1:1 petroleum ether−ethyl ether); ^{31}P NMR ($CDCl_3$) δ 127.2 (P−H, $^1J_{PH} = 331.8$ Hz); ^{1}H NMR ($CDCl_3$) δ 1.91 (OH), 3.61−3.76 (m, CH_2), 7.46−7.64 (m, 5H, Ph), 7.64 (d,

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[15] Khan, A. A.; Wismach, C.; Jones, P. G.; Streubel, R. *J. Chem. Soc., Dalton Trans.* **2003**, 2483.

[16] Appel, R.; Milker, R. *Z. Anorg. Allg. Chem.* **1975**, *417*, 161.

${}^1J_{P-H}$ = 331.8 Hz); ^{13}C NMR ($CDCl_3$) δ 62.18 (d, ${}^3J_{C-P}$ = 6.3 Hz, CH_2), 73.94 (d, ${}^2J_{C-P}$ = 14.6 Hz, CH_2), 129.20−135.64 (m, C ortho, meta, para), 204.79 (d, ${}^2J_{C-P}$ = 10.1 Hz, CO cis), 209.49 (d, ${}^2J_{C-P}$ = 27.2 Hz, CO trans); MS (FAB, ^{98}Mo) *m*/*z* 408 (M^+), 380 (M − CO, 34%), 352 (M − 2CO, 58%), 324 (M − 3CO, 18%), 268 (M − 5CO, 45%). Anal. Calcd for $C_{13}H_{11}MoO_7P$: C, 38.45; H, 2.73. Found: C, 38.81; H, 2.82.

***O*-Ethyl phenyltrichloromethylthiophosphinate (10).** The (7-phosphanobornadiene)pentacarbonylmolybdenum complex **1** (0.51 g, 0.9 mmol), 1-methylimidazole (0.58 mL, 7.2 mmol), and tetrachloromethane (0.70 mL, 7.2 mmol) were heated at 80 °C in toluene (5 mL) for 1 h (**8**, ^{31}P NMR δ 96.4). The mixture was cooled to room temperature, and ethanol (0.08 mL, 1.8 mmol) was added. The solution was stirred for a further 10 min and monitored by ^{31}P NMR (**9**, ^{31}P NMR δ 123.5). Sulfurization was performed by addition of sulfur powder (0.06 g, 1.8 mmol) at 40 °C for 1 day. After evaporation of the solvents, the residue was extracted with ethyl ether and purified by chromatography on silica gel with hexane as the eluent to yield 0.08 g (29%) of a bright yellow solid, **10**: R_f 0.2 (hexane); ^{31}P NMR ($CDCl_3$) δ 82.5; ^{1}H NMR ($CDCl_3$) δ 1.46 (t, ${}^3J_{H-H}$ 7.0 Hz, CH_3), 4.41−4.61 (m, CH_2), 7.44−8.16 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.35 (d, ${}^3J_{C-P}$ = 6.2 Hz, CH_3), 65.25 (d, ${}^3J_{C-P}$ = 6.2 Hz, CH_2), 96.83 (d, ${}^1J_{C-P}$ = 78.8 Hz, CCl_3), 127.96−134.09 (m, C ortho, meta, para); MS (EI) *m*/*z* 305 (MH^+). Anal. Calcd for $C_9H_{10}Cl_3OPS$: C, 35.61; H, 3.32. Found: C, 34.69; H, 3.90.

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