Direct Friedel-Crafts Acylation of Phosphole P-Mo(CO)$_5$ Complexes. A Simple Access to Functional Phospholes

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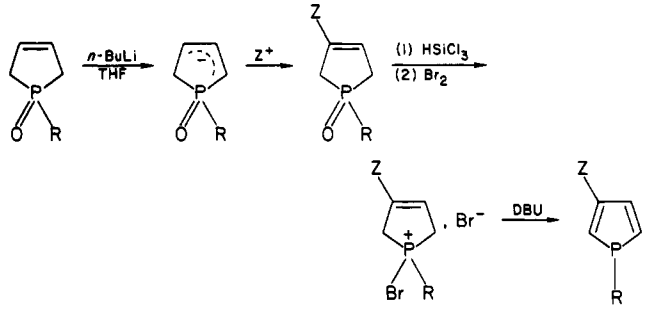
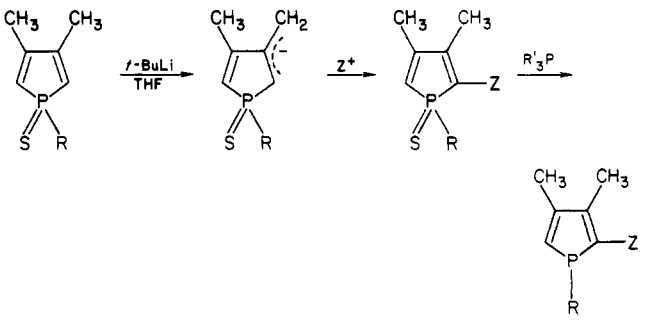
Direct Friedel-Crafts acylation of phosphole P(R)-Mo(CO)$_5$ complexes by R'C(O)Cl + $AlCl_3$ in refluxing carbon disulfide affords the corresponding C-acylated phosphole complexes. α-Acylation is very sensitive to steric hindrance and has only been demonstrated with the less bulky R and R' groups (R = Ph, Me; R' = Me). In other cases, β-acylation takes place instead, e.g., with R' = Ph. In one instance, a 2,4-diacetylation has been successfully performed. The decomplexation of the C-acyl phospholes thus obtained is achieved by reaction with trimethyl phosphite or carbon monoxide under pressure. Under similar acylation conditions, the phosphole P-Cr(CO)$_5$, -W(CO)$_5$, or -Fe(CO)$_4$ complexes mainly undergo P-decomplexation and not C-acylation.

Even though phospholes are now readily available,[1] the development of their chemistry is still hampered by the lack of a ready access to functional derivatives. Indeed, direct electrophilic functionalization of the phosphole ring at carbons is impossible due to the low aromaticity of the system[2] and to the high residual nucleophilicity of the phosphorus lone pair. Similarly, metalating agents such as *n*- or *tert*-butyllithium attack the phosphole ring at the phosphorus atom[3] and thus, C-metal derivatives remain unknown. Due to all these limitations, only two methods for preparing C-functional phospholes are presently known and both have serious drawbacks. The first one was proposed by Quin:[4]



R=Me; Z=C(O)OMe

In a first step, the functionality is installed on a phospholene oxide. Then, through subsequent reduction, P-bromination and dehydrobromination, the functional phospholene oxide is converted into the corresponding functional phosphole. Two unstable phosphole carboxylates have been prepared in low yield through such a scheme. Whereas this method has some generality, its complexity prevents its use for the synthesis of functional phospholes on a scale large enough for subsequent chemical studies. Another less complicated but less general synthesis of functional phospholes has been proposed by our laboratory:[5]



Z=C(O)Me, C(O)OEt, C(O)OH; R=*n*-Bu, *t*-Bu, Ph

In a first step, a monomeric 3,4-dimethylphosphole sulfide is reacted with *tert*-butyllithium at low temperature. Due to its steric bulk, *tert*-butyllithium attacks at the β-methyl substituent and gives a delocalized anion which reacts with some selected electrophiles to give α-functional phosphole sulfides; the quantitative reduction of these sulfides by a variety of trialkylphosphines then affords the requested functional phospholes. Although better than in the previous case, the overall yields remain low (ca. 20-30%) and the method is limited to the synthesis of 3,4-dimethyl-substituted α-functional phospholes. Thus, there is clearly a need for a simple, efficient, and general synthesis of functional phospholes. In the work described hereafter, we propose a partial answer to this problem.

Results and Discussion

Since electrophilic attack at the carbons of the phosphole dienic system is prevented by the reactivity of the phosphorus lone pair, an obvious idea was to block this lone pair by complexation with low-valent metals. These low-valent metals are known to render some electronic density to the phosphorus atom through π-backbonding[6] so that we could hope that the low aromaticity of the phosphole ring would not be entirely destroyed by the coordination of phosphorus.[7] In order to check this idea, we tried to perform electrophilic C-acetylations on a series of 3,4-dimethyl-1-phenylphosphole P complexes **1-4**. The acetylation reagent was CH_3COCl-$AlCl_3$ in dichloromethane or carbon disulfide. These experiments failed in all cases except **2**. Indeed, with the molybdenum complex, we achieved a rather clean C-acetylation. Other acylation

(1) The various syntheses of the phosphole ring have been reviewed recently: Quin, L. D. "The Heterocyclic Chemistry of Phosphorus"; Wiley-Interscience: New York, 1981. Since then, an optimized version of the simplest preparation of phospholes has been proposed: Brêque, A.; Mathey; F.; Savignac, P. *Synthesis* **1981**, 983.

(2) A thorough discussion on phosphole aromaticity is presented in the following: Mathey, F. *Top. Phosphorus Chem.* **1980**, *10*, 1. Since the publication of this review, no new experimental evidence needs a reappraisal of this question.

(3) Mathey, F. *Tetrahedron* **1972**, *28*, 4171.

(4) Quin, L. D.; Borleske, S. G. *Tetrahedron Lett.* **1972**, 299. Quin, L. D.; Borleske, S. G.; Engel, J. F. *J. Org. Chem.* **1973**, *38*, 1858.

(5) Mathey, F. *Tetrahedron Lett.* **1973**, 3255; *Tetrahedron* **1974**, *30*, 3127; *Tetrahedron*, **1976**, *32*, 2395.

(6) On the basis of XPS experiments, it has been demonstrated that phosphorus remains practically neutral in tertiary phosphine complexes: Chatt, J.; Leigh, G. J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 400.

(7) On the basis of X-ray structural data, it has been suggested that some electronic cyclic delocalization is still operative in phosphole P complexes, see: Mac Dougall, J. J.; Nelson, J. H.; Mathey, F.; Mayerle, J. J. *Inorg. Chem.* **1980**, *19*, 709.

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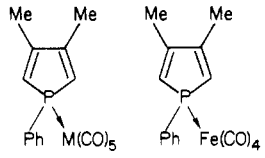

1, M = Cr
2, M = Mo
3, M = W

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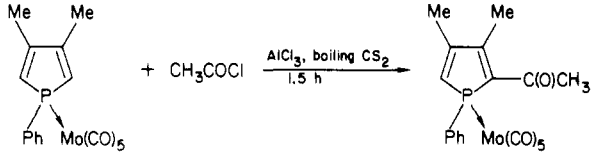
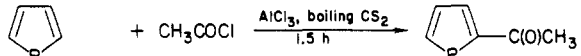


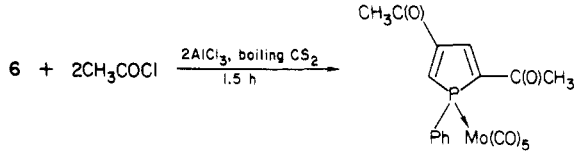
2 5 (51% yield)

catalysts such as BF_3–Et_2O proved to be ineffective. The specificity of molybdenum was rather puzzling at first. However, a closer inspection of the various reactions showed that a highly competitive decomplexation of the phosphole ligand took place in the case of **1**, **3**, and **4**. P-decomplexation in similar $R_3P \rightarrow M$ complexes through transient aluminum trihalide coordination to the trans carbonyl group of the metallic moiety has been already demonstrated when M = $W(CO)_5$[8] and M = $Fe(CO)_4$.[9] Thus, the specificity of molybdenum in these phosphole acylation experiments probably reflects a lower basicity of the trans carbonyl group in the $LMo(CO)_5$ complex by comparison with the $LCr(CO)_5$, $LW(CO)_5$, and $LFe(CO)_4$ corresponding species and, thus, a better stability of $LMo(CO)_5$ toward $AlCl_3$. This hypothesis will be further supported by another fact described later.

After this preliminary success, we checked if it was possible to suppress the 3,4-dimethyl substitution on the phosphole ring. This was indeed the case, since the 1-phenylphosphole complex **6** was acetylated under the same experimental conditions as those used for **2**. The acetylation takes place on the α-position as demonstrated by the ^{13}C NMR spectrum of **7**: the magnitude of the ^2J(CO···P) coupling (12.2 Hz) is practically identical with the value recorded for **5**. We also discovered that, when using an excess of the acylation reagent, it was possible to perform a diacetylation. The ^1H NMR spectrum of **8** shows



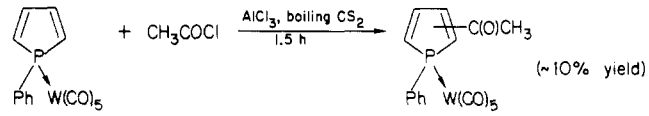
6 7 (~36% yield)



8 (~30% yield)

two different $COCH_3$ at 2.46 and 2.55 ppm in $CDCl_3$ thus implying a disymmetrical disubstitution. The magnitude of the coupling between the two ring protons (1.46 Hz) excludes the 2,3-diacetyl isomer.

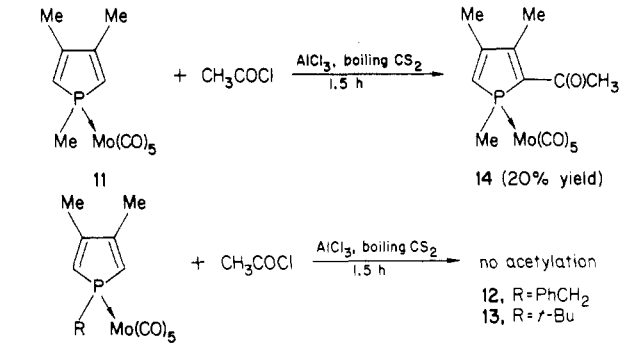
We also performed an acetylation experiment with the tungsten analogue of complex **6**. Contrary to the failure observed with the 3,4-dimethyl-substituted tungsten complex **3**, we were able to functionalize the unsubstituted phosphole ring of **9**, although in low yield. Complex **10**



9 10 (~10% yield)

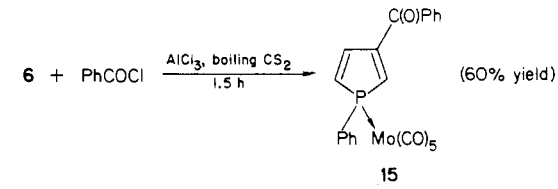
was obtained in low quantities, so that we were unable to record its ^{13}C NMR spectrum. Thus, we cannot assign a precise formula to **10**. However, in view of the similarities between the ^1H NMR spectra of **7** and **10**, α-acetylation appears likely in **10**. It is well-known that 3,4-dimethyl substitution drastically enhances the basicity of phospholes.[2] When passing from **3** to **9**, the suppression of this substitution probably lowers the basicity of the trans carbonyl group in the $P \rightarrow W(CO)_5$ moiety and reduces its coordinating ability toward $AlCl_3$. Thus, the functionalization is favored against the decomplexation.

Then, we checked the influence of the substituent at phosphorus upon the acylation reaction. The phenyl group of **2** was successively replaced by a methyl (complex **11**), a benzyl (complex **12**), and a *tert*-butyl group (complex **13**). In the case of **12** and **13**, a combination of two adverse effects, higher steric crowding of the α-positions and higher basicity than in **2**, precluded the C-acetylation. In the case of **11**, the low steric crowding allowed the reaction to take place although in lower yield than with **2** probably because of the higher tendency to decomplexation. In order to further generalize our initial result, we then attempted an electrophilic benzoylation on complex **2**. To our surprise, no benzoylation took place under a variety of conditions. Since we suspected once again an adverse steric effect (due to the acylating agent in that case), we attempted the benzoylation of the C-unsubstituted complex **6**. The benzoylation cleanly took place on the β-position, thus supporting the steric interpretation of our preceding failure. The ^{13}C NMR spectrum of complex **15** shows the ketonic carbonyl as a singlet, thus demonstrating unambiguously the β-acylation Similar β-acylations have been performed on pyrroles with some selected bulky N-substituents.[10]



11 14 (20% yield)

12, R = $PhCH_2$
13, R = *t*-Bu



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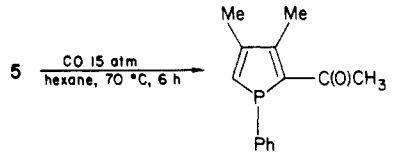
Other attempted generalizations include Vilsmeier formylation with $P(O)Cl_3$ and HC(O)N(Me)Ph either in re-

(8) Ben Taarit, Y.; Bilhou, J. L.; Lecomte, M.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1978**, 38.
(9) Santini, C. C.; Mathey, F. *J. Organometal. Chem.* **1984**, *266*, 285.
(10) Kakushima, M.; Hamel, P.; Frenette, R.; Rokach, J. *J. Org. Chem.* **1983**, *48*, 3214.

fluxing CS_2 or in $P(O)Cl_3$ as a solvent at 106 °C and carboxamidation with $AlCl_3$ and $Ph_2NC(O)Cl$ either in refluxing CS_2 or without solvent at 120 °C for 4.5 h. In all cases, we observed either the absence of reaction or the decomposition of the products.

The last problem remaining to be solved was the decomplexation of the acylated phospholes. This decomplexation was studied in the case of complex **5**. It must be stressed here that acylated phospholes are very poor ligands. This was clearly shown in one instance: the reaction of iron carbonyls with phosphine sulfides R_3PS is known to produce $R_3P \rightarrow Fe(CO)_4$ complexes;[11] a similar reaction attempted with 2-acetyl-3,4-dimethyl-1-phenylphosphole sulfide afforded the tervalent phosphole instead of its complex.[5] On this basis, we tried to displace the functional phosphole from the coordination sphere of molybdenum by other more powerful ligands including CO and $P(OMe)_3$. The decomplexation of **5** can be performed in ca. 50% yield by heating this complex under CO pressure. The free phosphole **16** has already been described



16

in the literature.[5] The decomplexation is very clean but never complete. The separation of **16** and **5** is achieved by chromatography on silica gel. Trimethyl phosphite also displaces **16** from its complex. The reaction goes to completion in 1.5 h in refluxing benzene. The purification of **16** is somewhat more difficult because the reaction is less clean than in the first case.

This collection of data shows conclusively that direct acylation of phosphole $P \rightarrow Mo(CO)_5$ complexes is a simple and rather efficient synthesis of functional phospholes. Optimization of the acylation and decomplexation steps is still possible.

Experimental Section

All reactions were performed under argon. Molecular weights were measured on a VG 30F mass spectrometer at 70 eV. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker WP 80 spectrometer at 80.13 MHz for ^1H, 32.435 MHz for ^{31}P, and 20.15 MHz for ^{13}C. ^{31}P chemical shifts are externally referenced to 85% H_3PO_4; ^1H and ^{13}C chemical shifts are internally referenced to Me_4Si and are positive for downfield shifts in all cases. IR spectra were obtained on a Perkin Elmer 257 instrument. Elemental analyses were performed by "Service Central de Microanalyse du CNRS". Chromatographic separations were performed on silica gel columns (70–230 mesh). Complexes **1**, **3**, **4**, and **9** were made as described in the literature.[12a] Complexes **2** and **6** were synthesized by a special procedure and isolated in satisfactory yields (usually 75–85%). Dry trimethylamine *N*-oxide was added by portions to an equimolecular mixture of $Mo(CO)_6$ and phosphole in CH_2Cl_2 at 20 °C; gas evolved immediately; after 30 min of stirring, the reaction mixture was filtered on Celite and the solvent was evaporated; then the residue was chromatographed with hexane as the eluent [$R_f = 0.5$]. Physical constants were identical with those previously described.[12b]

General Procedure for the Acylation of Phosphole Complexes. [2-Acetyl-3,4-dimethyl-1-phenylphosphole]pentacarbonylmolybdenum (5). To 20 mL of dry carbon disulfide was added 1.2 mL (10 mmol) of freshly distilled acetyl chloride and 1.2 g (9.56 mmol) of anhydrous aluminum chloride. The mixture was stirred for 10 min at room temperature. Then 3 g (6.86 mmol) of **2** dissolved in 50 mL of carbon disulfide was added. The reaction mixture was stirred for an additional 1.5 h at 45 °C, and after cooling, 50 mL of dichloromethane was added. Then, the reaction mixture was rapidly poured into a stirred mixture of 25 mL of 28% aqueous ammonia and 30 g of ice; after 5 min, the layers were separated. The organic layer was washed with saturated NH_4Cl solution and was dried ($MgSO_4$). The solvent was removed leaving a red oil which was chromatographed on silica gel with hexane:ethyl ether (4:1) as the eluent; 0.8 g of starting material was recovered and 1.2 g [$\rho = 51\%$] of **5** was obtained as a deep orange oil which crystallized in pentane at −25 °C: mp 92 °C. Anal. Calcd for $C_{19}H_{15}MoO_6P$: C, 48.94; H, 3.24; P, 6.64. Found: C, 48.81; H, 3.00; P, 6.62. IR (decalin) ν (C≡O) 2065 m, 1948 s, ν(C=O) 1625 cm^{-1} (KBr); ^1H NMR ($CDCl_3$) δ 2.23 [d, $^4J_{PH}$ = 1.2 Hz, CH_3C], 2.30 [d, $^4J_{PH}$ = 1.2 Hz, CH_3C], 2.49 [s, $CH_3C(O)$], 6.76 [d, $^2J_{PH}$ = 35.4 Hz, =CH], 7.39–7.41 [m, C_6H_5P]; ^{31}P NMR ($CDCl_3$) δ 34.27; ^{13}C NMR (C_6D_6) δ 31.50 (C(O)Me), 193.62 [d, $^2J_{PC}$ = 14.6 Hz, C(O)Me], 206.25 [d, $^2J_{PC}$ = 8.5 Hz, CO cis]; mass spectrum (EI, ^{98}Mo), *m/e* 440 [M − CO, 2], 4.12 [M − 2CO, 1.4], 384 [M − 3CO, 3.2], 356 [M − 4CO, 2.3], 328 [M − 5CO, 18.4], 230 [L, 77], 188 [L − $COCH_2$, 85].

[2-Acetyl-1-phenylphosphole]pentacarbonylmolybdenum (7): mp (pentane) 87–88 °C; ρ = 36%. Anal. Calcd for $C_{17}H_{11}MoO_6P$: C, 46.59; H, 2.53; P, 7.07. Found: C, 47.05; H, 2.46; P, 7.29. IR (hexane) ν(C≡O) 2068 m, 1950 vs, ν(C=O) 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 [d, $^4J_{PH}$ = 0.73 Hz, $CH_3C(O)$]; ^{31}P NMR ($CDCl_3$) δ 39.38; ^{13}C NMR ($CDCl_3$) δ 26.3 [d, $^3J_{PC}$ = 3.6 Hz, $CH_3C(O)$], 135.58 [d, $^2J_{PC}$ = 4.88 Hz, C_4], 143.6 [d, $^2J_{PC}$ = 8.5 Hz, C_3], 144.6 [d, $^1J_{PC}$ = 26.9 Hz, C_5], 151.7 [d, $^1J_{PC}$ = 34.18 Hz, C_2], 192.6 [d, $^2J_{PC}$ = 12.20 Hz, *C*(O)Me], 204.67 [d, $^2J_{PC}$ = 8.54 Hz, CO cis], 209.0 [d, $^2J_{PC}$ = 20.75 Hz, CO trans]; mass spectrum [DCI, NH_3^+, ^{98}Mo], *m/e* 441 [M + 1, 12], 412 [M − CO, 100].

[2,4-Diacetyl-1-phenylphosphole]pentacarbonylmolybdenum (8): mp (pentane) 97–98 °C; ρ = 30%; IR (hexane) ν(C≡O) 2070, 1950 vs, ($CDCl_3$) ν(C=O) 1682 and 1663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 [d, $^4J_{PH}$ = 1.0 Hz, $CH_3C(O)C_2$], 2.55 [s, $CH_3C(O)C_4$], 7.81 [ABX, $^4J_{HH}$ = 1.46 Hz, $^2J_{PH}$ = 32.3 Hz, HC_5], 7.96 [*A*BX, $^4J_{HH}$ = 1.46 Hz, $^3J_{PH}$ = 24.2 Hz, HC_3]; ^{31}P NMR ($CDCl_3$) δ 50.07; mass spectrum [DCI, NH_3^+, ^{98}Mo], *m/e* 500 [M + 1 + NH_3, 16.6], 483 [M + 1, 7], 469 [483 − CH_2, 33.5], 262 [L + 1 + NH_3, 52], 245 [L + 1, 25].

[Acetyl-1-phenylphosphole]pentacarbonyltungsten (10): orange oil; $\rho \sim 10\%$; IR (neat) ν(C≡O) 2060 m, 1945 vs, ν(C=O) 1658 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 [d, $J_{PH} \sim 1$ Hz, $CH_3C(O)$]; ^{31}P NMR δ 20.42, $^1J_{PW}$ = 212.4 Hz; mass spectrum [DCI, NH_3^+, ^{184}W], *m/e* 527 [M + 1, 95], 498 [M − CO, 100].

[2-Acetyl-1,3,4-trimethylphosphole]pentacarbonylmolybdenum (14): yellow oil; ρ = 20%; IR (hexane) ν(C≡O) 2060 m, 1950 vs, (neat) ν(C=O) 1642 cm^{-1}; ^1H NMR [($CDCl_3$/C_6D_6) (3:1)] δ 1.39 [d, $^2J_{PH}$ = 8 Hz, CH_3P], 1.67 [d, $^4J_{HH}$ = 1.5 Hz, CH_3C_4], 1.79 [s, CH_3C_3], 2.15 [d, $^4J_{PH}$ = 0.8 Hz, $CH_3C(O)$], 6.23 [d, $^2J_{PH}$ = 35.89 Hz, =CH]; ^{31}P NMR ($CDCl_3$) δ 22.0; ^{13}C NMR ($CDCl_3$) δ 14.17 [d, $^1J_{PC}$ = 21.97, CH_3P], 16.56 [d, $^3J_{PC}$ = 6.91, CH_3C], 17.77 [d, $^3J_{PC}$ = 8.54, CH_3C], 31.02 [s, *C*$H_3C(O)$], 137.09 [d, $^1J_{PC}$ = 34.18, =CH]; mass spectrum [DCI, NH_3^+, ^{98}Mo], *m/e* 407 [M + 1, 7], 378 [M − CO, 100].

[3-Benzoyl-1-phenylphosphole]pentacarbonylmolybdenum (15): pale yellow solid; $\rho \sim 60\%$; mp 123 °C; IR ($CDCl_3$) ν(C≡O) 2060 m, 1942 vs, ν(C=O) 1657 cm^{-1}; ^{31}P NMR ($CDCl_3$) 57.37 ppm; ^{13}C NMR ($CDCl_3$) δ 136.28 [d, $^2J_{PC}$ = 6.1 Hz, C_4], 138.04 [d, $^2J_{PC}$ = 18.3 Hz, C_3], 141.61 [d, $^1J_{PC}$ = 37.8 Hz, C_5], 142.70 [d, $^1J_{PC}$ = 35.4 Hz, C_2], 190.05 [s, *C*(O)Ph], 205.13 [d, $^2J_{PC}$ = 9.77 Hz, CO cis], 209.64 [d, $^2J_{PC}$ = 23.2 Hz, CO trans]; mass spectrum [DCI, NH_3^+, ^{98}Mo], *m/e* 519 [M + 1 + NH_3, 52], 503 [M + 1, 65], 447 [M − 2CO, 100].

Acknowledgment. We thank Dr. C. Charrier for recording the ^{13}C NMR spectra.

Registry No. **2**, 74363-92-1; **5**, 94024-73-4; **6**, 74391-00-7; **7**, 94024-74-5; **8**, 94024-75-6; **9**, 94024-76-7; **10**, 94024-77-8; **11**, 74363-93-2; **14**, 94024-78-9; **15**, 94024-79-0; **16**, 62451-14-3; $Mo(CO)_6$, 13939-06-5; $AlCl_3$, 7446-70-0; CH_3COCl, 75-36-5; PhCOCl, 98-88-4; $P(OMe)_3$, 121-45-9; CO, 630-08-0; trimethylamine *N*-oxide, 1184-78-7; phosphole, 288-01-7.

(11) Mercier, F.; Mathey, F.; Angenault, J.; Couturier, J. C.; Mary, Y. *J. Organometal. Chem.* **1982**, *231*, 237.

(12) (a) Mathey, F.; Fischer, J.; Nelson, J. H. "Structure and Bonding"; Springer Verlag: Berlin, 1983; Vol. 55, p 153. (b) Santini, C. C.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 5809.