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Preliminary communication

Controllable migration of acyl groups from molybdenum to phosphido ligands: synthesis of acylphosphine complexes

Peter Blenkiron, Mark H. Lavender and Michael J. Morris
Department of Chemistry, University of Sheffield, Sheffield S3 7HF (UK)

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Abstract

Deprotonation of the diphenylphosphine ligand of $[CpMo(CO)_2(PPh_2H)(COR)]$ ($Cp = \eta^5\text{-}C_5H_5$, R = Me, Et) with DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) at −78°C followed by treatment with R′I (R′ = Me, Et) leads to the substituted phosphine acyl complexes $[CpMo(CO)_2(PPh_2R')(COR)]$; if the deprotonation is carried out at room temperature, however, migration of the acyl group to the phosphorus atom occurs to give the acylphosphine alkyl complexes $[CpMo(CO)_2(PPh_2COR)(R')]$ after alkylation with R′I.

We are currently investigating a number of carbon–phosphorus bond formation and bond cleavage reactions at transition metal centres. Such processes are known to be involved in the deactivation of phosphine-containing catalyst systems such as Wilkinson's catalyst [1], but they may also prove useful for the template construction of phosphorus ligands which are otherwise difficult to prepare. Part of this work is concerned with the interaction of phosphido ligands ($-PR_2$) with organic substrates. The presence of a lone pair on the phosphorus atom renders it nucleophilic, and enables it to participate in such reactions as alkylation, oxidation, phosphido-bridge formation with suitable metal fragments [2], and coupling with electrophilic alkynes to form metallacycles [3].

The reactivity of metal acyl complexes is also of considerable interest given their importance in industrial catalytic cycles and, more recently, in organic synthesis. In this Communication we report the migration of acyl ligands from a metal centre to a coordinated phosphido group to form acylphosphine complexes. Such complexes are not numerous, and have previously been prepared by reaction of suitably labile precursors with free acylphosphines [4], or by acetylation of anionic phosphido ligands with acetyl chloride [5]. There are also several cases of the formation of metallacycles through attack of phosphine ligands on acyl groups [6], but to our knowledge no previous examples of acyl to phosphido migration. Interestingly it

Correspondence to: Dr. M.J. Morris, Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK.

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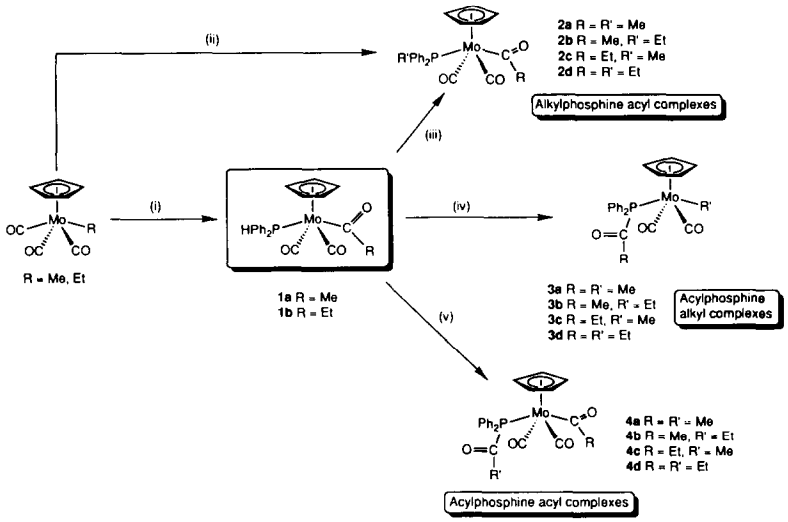


Scheme 1. Deprotonation reactions of $[CpMo(CO)_2(PPh_2H)(COR)]$. Reagents and conditions: (i) PPh_2H in MeCN, 18 h; (ii) PPh_2R' in MeCN, 18 h; (iii) DBU in THF at −78°C, 30 min, then R'I, warm to r.t., stir for 18 h; (iv) DBU in THF, r.t., 30 min, then R'I, stir for 18 h; (v) DBU in THF, −78°C, 30 min, then R'COCl at −78°C, stir cold for 2 h.

has been reported that acylphosphines are decarbonylated to alkylphosphines by Wilkinson's catalyst, a reaction which is assumed to involve the reverse process, but this occurs only at 120°C [7].

As shown in Scheme 1, our synthetic routes use the simple precursor complexes $[CpMo(CO)_2(PPh_2H)(COR)]$ (**1a**, R = Me; **1b**, R = Et). Like their PPh_3 analogues, these are readily prepared by stirring $[CpMo(CO)_3R]$ with PPh_2H at room temperature in acetonitrile overnight [8]; their spectroscopic properties [9*] are in complete accord with the proposed structures.

Deprotonation of the phosphine ligand of **1** proceeds smoothly with DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) at −78°C in THF to give an anionic species which is presumed to be the phosphido complex $[CpMo(CO)_2(PPh_2)(COR)]^-$. On addition of R'I (R' = Me or Et) and warming to room temperature, the substituted phosphine acyl complexes $[CpMo(CO)_2(PPh_2R')(COR)]$ (**2a–d**) are produced in excellent yields (> 80%). This simple deprotonation/alkylation sequence parallels those observed earlier by Treichel [10]. To confirm their identities, these compounds were also synthesized independently by reaction of the appropriate $[CpMo(CO)_3R]$ with PPh_2Me or PPh_2Et in MeCN [8]. Table 1 shows selected spectroscopic data for R = R' = Me, which are virtually identical to those reported previously.

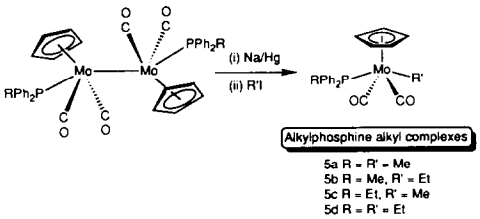
If the deprotonation reaction is carried out at room temperature (or if the low-temperature solution above is stirred at room temperature for a while before

* Reference number with asterisk indicates a note in the list of references.

Table 1

Selected spectroscopic data for complexes with R = R′ = Me. IR (cm^{-1}) in CH_2Cl_2 solution, NMR (δ in ppm, J in Hz) in $CDCl_3$ solution, Ph and Cp omitted

Compound	IR	^{1}H NMR	^{13}C NMR	^{31}P NMR
[CpMo(CO)$_2$(PPh$_2$Me)Me]	1929m	2.11 (d, *J* 8.0, PMe)	21.5 (d, *J* 34, PMe)	53.7
(5a)	1842s	0.35 (d, *J* 2.5, MoMe)	−19.6 (d, *J* 10, MoMe)	
[CpMo(CO)$_2$(PPh$_2$Me)(COMe)]	1934m	2.59 (s, MoCOMe)	266.7 (d, *J* 11, MoCOMe)	49.5
(2a)	1849s	2.20 (d, *J* 8.5, PMe)	51.3 (s, CO*Me*)	
	1601br		20.5 (d, *J* 34, PMe)	
[CpMo(CO)$_2$(PPh$_2$COMe)Me]	1937m	2.27 (d, *J* 4.0, PCOMe)	212.9 (d, *J* 15, PCOMe)	82.5
(3a)	1855s	0.44 (d, *J* 2.5, MoMe)	30.3 (d, *J* 43, PCO*Me*)	
	1686w		−18.8 (d, *J* 9, MoMe)	
[CpMo(CO)$_2$(PPh$_2$COMe)(COMe)]	1939m	2.66 (s, MoCOMe)	263.3 (d, *J* 10, MoCOMe)	77.0
(4a)	1858s	2.42 (d, *J* 4.3, PCOMe)	211.9 (d, *J* 15, PCOMe)	
	1690w		51.2 (s, MoCO*Me*)	
	1623w		30.8 (d, *J* 44, PCO*Me*)	



Scheme 2. Synthesis of alkylphosphine alkyl complexes.

alkylation), the addition of R'X gives different products, again in excellent yield. These four compounds **3a–d** were identified as the acylphosphine alkyl complexes $[CpMo(CO)_2(PPh_2COR)(R')]$ on the basis of their spectroscopic data. We therefore conclude that at room temperature migration of the acyl ligand to the phosphido group occurs, giving the anion $[CpMo(CO)_2(PPh_2COR)]^-$. Presumably the acyl migration occurs from a *cis* position, though the NMR spectra of **1a** and **1b** show exclusively *trans* isomers (*cis–trans* isomerization is known to be easy in four-legged piano-stool systems such as these [11*]).

Reaction of the molybdenum-centred anions derived by the room temperature deprotonation of $[CpMo(CO)_2(PPh_2H)(COR)]$ with the acyl chlorides R'COCl led to a mixture of products, including the hydride complexes $[CpMo(CO)_2(PPh_2COR)(H)]$. However, the phosphorus-centred anions derived from low-temperature deprotonation of **1** reacted cleanly to give the acylphosphine acyl complexes $[CpMo(CO)_2(PPh_2COR')(COR)]$ (**4a–d**) in yields of over 80%. Relevant spectroscopic properties of the R = R' = Me derivative are shown in Table 1.

In order to complete a series of related complexes, we also prepared the related alkylphosphine alkyl species $[CpMo(CO)_2(PPh_2R)(R')]$ (**5a–d**) by cleavage of the substituted dimers $[CpMo(CO)_2(PPh_2R)]_2$ with sodium amalgam and alkylation of the resulting anion with R'X [11*,12*] (Scheme 2). The data for R = R' = Me are shown in Table 1.

Examination of Table 1 shows that the acylphosphine complexes such as **3a** can be distinguished from their alkylphosphine counterparts in several ways. Firstly, the IR spectrum in CH_2Cl_2 shows a rather weak acyl peak at *ca.* 1685 cm^{-1}, together with the two strong CO absorptions indicative of a *trans*-configuration of the CO ligands. Secondly, the ^{31}P NMR spectrum comprises a singlet at around 80 ppm, a difference in chemical shift of approximately 30 ppm compared to PPh_2Me complexes such as **2a**. Thirdly, the presence of the acylphosphine ligand is confirmed by the ^{13}C NMR spectrum which contains a doublet at about 212 ppm (J = *ca.* 15 Hz) due to the acyl carbon. As shown in Table 1, acyl ligands bound to molybdenum such as that in **2a** resonate at much lower field, *ca.* 270 ppm.

In conclusion the controllable migration or non-migration of the acyl ligand provides a convenient method for the synthesis of a wide range of alkyl and acyl complexes, and we are currently exploring the mechanism and scope of the reaction both with molybdenum and other metals.

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9 Selected spectroscopic data (IR in CH_2Cl_2, NMR in $CDCl_3$, coupling constants in Hz): **1a**: IR 1940m, 1856s, 1618br cm^{-1}; ^1H NMR: δ 7.08 (d, J 361, 1H, P-H), 2.60 (s, 3H, Me); ^{13}C NMR δ 265.6 (d, J 11, acyl CO), 51.4 (s, Me); ^{31}P NMR 41.3 ppm. **1b**: IR 1938m, 1853s, 1614w cm^{-1}; ^1H NMR δ 7.07 (d, J 360.4, 1H, P-H), 2.98 (q, J 7.4, 2H, CH_2), 0.88 (t, 3H, CH_3); ^{13}C NMR δ 267.3 (d, J 12, acyl CO), 58.2 (s, CH_2), 9.9 (s, CH_3); ^{31}P NMR 41.9 ppm. All the complexes described in this paper were isolated as yellow air-stable solids which gave satisfactory analytical data.

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