Journal of Organometallic Chemistry, 149 (1978) C29—C33
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary Communication

STABLE ALLYL-PHOSPHONIUM AND -PYRIDINIUM COMPLEXES OF MOLYBDENUM

J.A. McCleverty* and A.J. Murray

Department of Chemistry, The University, Sheffield S3 7HF, England.

(Received February 8th, 1978)

Summary

The synthesis and characterisation of $[Mo(\eta^5-C_5H_5)(\eta^2-C_3H_5L)(CO)(NO)]^+$ (L = tertiary phosphine or pyridine) is described, and the reactions of $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)(NCMe)(NO)]^+$ with C_5H_5N and $4-MeC_5H_4N$ (L), which gave either $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)L(NO)]^+$ (L = C_5H_5N) or $[Mo(\eta^5-C_5H_5)(\eta^2-C_3H_5L)(NCMe)(NO)]^+$ (L = $4-MeC_5H_4N$), are reported.

The formation of metal-stabilised C-phosphonium or -pyridinium salts by addition of PR_3 or pyridines to the hydrocarbon ligand in cationic metal complexes is a relatively rare phenomenon. The few examples where such compounds have been obtained have largely involved cyclic diene, dienyl or trienyl species,[1] and there appear to be only two examples where addition of a phosphine or pyridine to acyclic hydrocarbon metal compounds has resulted in the formation of isolable metal-containing phosphonium or pyridinium complexes. These are (i) addition of PR_3 (R = Ph or OPh) to $[Fe(\eta^5-C_5H_5)(\eta^2-C_2H_3R')(CO)_2]^+$ (R' = Me or Ph)[2] in which $[Fe(\eta^5-C_5H_5)(CH_2CHR'PR_3)(CO)_2]^+$ was formed, and (ii) production of $[Fe(\eta^2-C_3H_4RL)(CO)_4]^+$ from $[Fe(\eta^3-C_3H_4R)(CO)_4]^+$ and L (PR'_3 or pyridine).[3] Indeed, in this last case, only the complex where R = H and R' = Ph was actually isolated, in all other instances only the appropriate organic phosphonium or pyridinium salts being recovered.

It has been proposed, however, that allyl-phosphonium salts, possibly attached to the metal, are involved when the hydrocarbon is removed by PR_3 from allyl palladium(II) complexes[4] and $Mo(\eta^3-C_3H_5)(CO)_2(NCMe)_2X$.[5]

In this communication we describe the isolation and characterisation of stable allyl-phosphonium and -pyridinium salts containing the group $\{Mo(\eta^5-C_5H_5)(CO)(NO)\}$. Thus, treatment of $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)(CO)(NO)][PF_6]$[6] with tertiary phosphines, pyridine or methylpyridines (PEt_3, $PBu^n{}_3$, PPh_3, $PHPh_2$, $PPhMe_2$, C_5H_5N, 2-, 3- or $4-MeC_5H_4N$) afforded the yellow complexes $[Mo(\eta^5-C_5H_5)(C_3H_5L)(CO)(NO)][PF_6]$ in good yields.

Our formulation of these compounds as metal-containing phosphonium or pyridinium salts, i.e. 1, rather than as η^1-allylic cations having 3:4 coordination at the metal, i.e. 2, is based on the following considerations:

(a) The NO stretching frequencies of the compounds $[Mo(\eta^5-C_5H_5)(C_3H_5L)(CO)(NO)]^+$ (average ca. 1625 cm^{-1}) are closer to the values obtained from the neutral species $Mo(\eta^5-C_5H_5)(\eta^2-C_3H_5Q)(CO)(NO)$ (Q = H, OH, OMe, SEt, SCOMe, etc.; between 1605 and 1620 cm^{-1})[6] than to the values obtained from cationic complexes such as $[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)L(NO)]^+$ and $[Mo(\eta^5-C_5H_5)I(NO)L_2]^+$ [7] (see Table 1).

(b) The ^1H n.m.r. spectra of the phosphine- and pyridine-containing complexes exhibit a singlet cyclopentadienyl proton resonance (no J_{PH}) at a chemical shift (ca. δ5.72) more typical of neutral cyclopentadienyl allyl nitrosyl compounds than of their cationic counterparts (Table 1). Unfortunately, because of solubility difficulties, we were unable to satisfactorily resolve the signals due to the allyl group, or to obtain ^{13}C n.m.r. spectra.

(c) Metal-bound phosphonium salts should exhibit ^{31}P n.m.r. chemical shifts in the same region as the corresponding 'free' allyl phosphonium salts since the P atom is at some distance from the metal in 1 and is unlikely to be much affected by it. A tertiary phosphine bound directly to Mo, however, would be expected to show significantly different ^{31}P n.m.r. chemical shifts. Accordingly, δ_P for $[PEt_3(C_3H_5)]^+$ and for $[PPhMe_2(C_3H_5)]^+$ (PEt_3R^+ and $PPhMe_3R^+$ representing convenient extremes in the range of ^{31}P n.m.r. chemical shifts for tertiary

Table 1: IR and ^{1}H n.m.r. spectral data

Complex[a]		ν(CO),ν(NO)[b]	$\delta(C_5H_5)$[c]
$[Mo(\eta^5-C_5H_5)(\eta^2-C_3H_5L)(CO)(NO)]^+$;	L = PEt_3	1971, 1623	5.74
	L = PPh_3	1981, 1629	5.71
	L = $PPhMe_2$	1980, 1628	5.70
	L = C_5H_5N	1984, 1619	5.81
	L = 4-MeC_5H_4N	1987, 1628	5.74
$[Mo(\eta^5-C_5H_5)I(NO)L_2]^+$;	L = PMe_2Ph	1652	5.98(t;J_{HP}3.0Hz)
$Mo(\eta^5-C_5H_5)(\eta^2-C_3H_5Q)(CO)(NO)$;	Q = H	1959, 1619	5.58
	Q = OH	1950, 1607	5.47
	Q = SEt	1980, 1608	5.52
	Q = SCOMe	1981, 1620	5.59
$[Mo(\eta^5-C_5H_5)(\eta^3-C_3H_5)L(NO)]^+$;	L = CO	1095, 1727	6.45,6.29[d]
	L = NCMe	1671	6.29,6.14[d]
$Mo(\eta^5-C_5H_5)(CO)(NO)(PPh_3)$		1978, 1628	e

[a] $AsPF_6^-$ salts where appropriate; [b] in KBr discs; [c] in $(CD_3)_2CO$ vs TMS at 100 MHz; [d] Two isomers determined by the orientation of the allyl group with respect to the η-C_5H_5 ring; [e] insufficiently soluble.

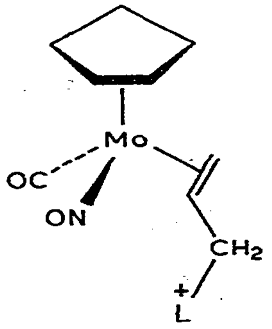
phosphonium salts) were compared with those obtained from the corresponding Mo complexes (Table 2). The differences between δ_P for each organometallic species and its corresponding 'free' phosphonium salt were only 0.567 ppm (PEt_3R^+) and 0.085 ppm ($PPhMe_2R^+$) respectively, whereas the difference between the shifts of the two 'free' salts was of the order of 15 ppm.

Accordingly, we feel satisfied that the complexes $[Mo(\eta^5-C_5H_5)(C_3H_5L)(CO)(NO)]^+$ should be represented as in 1.

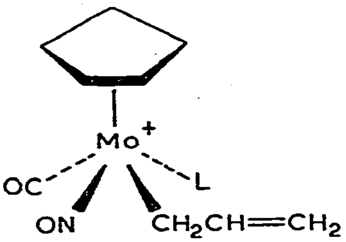
Table 2: ^{31}P n.m.r. spectral data

Complex^{a}	$_{p}$(ppm)^{b}
$[Mo(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_3H_5PEt_3)(CO)(NO)]^+$	-15.283
$[PEt_3(C_3H_5)]^+$	-15.850
$[Mo(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_3H_5PPhMe_2)(CO)(NO)]^+$	-30.071
$[PPhMe_2(C_3H_5)]^+$	-29.986

[a] As PF_6^- salts; [b] ^{1}H decoupled; in CH_2Cl_2 solution, recording using Jeol PFT 100 spectrometer, vs. H_3PO_4 as external reference (PF_6^- resonance observed but not quoted).



(1)



(2)

Abstraction of iodide ion from $Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)I(NO)$, using $AgPF_6$ in acetonitrile, afforded $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(NCMe)(NO)]^+$. Treatment of this cation with pyridine gave the yellow $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(NC_5H_5)(NO)]^+$, but with $4\text{-}MeC_5H_4N$, the reaction followed a different course. Thus, an i.r. spectrum of the crude reaction product revealed only one NO stretching frequency with a value typical of a neutral nitrosyl allyl complex, and also ν(CN) due to a coordinated acetonitrile molecule. Thus we believe that the species $[Mo(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_3H_5L)(NCMe)(NO)]^+$ (L = $4\text{-}MeC_5H_4N$) was formed. However, our attempts to purify this salt led to its decomposition and isolation of only $[4\text{-MeC}_5H_4NC_3H_5][PF_6]$. Similar results were obtained with PPh_3 and $P(OPh)_3$.

However, when $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(CO)(NO)]^+$ was treated with PPh_3 in the presence of NaOEt, $Mo(\eta^5\text{-}C_5H_5)(CO)(NO)(PPh_3)$ was formed. We suggest that this reaction occurs via ethoxide ion attack on the allyl group, giving the intermediate $Mo(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_3H_5OEt)(CO)(NO)$ (the corresponding methoxide has been obtained by treatment of the carbonyl cation with NaOMe), and that the vinyl ether is then displaced from this by PPh_3 giving the observed product.

We are grateful to the SRC for a studentship, to Mrs. J. Warrington and Mr. A. Jones for technical assistance, and to Dr. B.E. Mann and Dr. B.F. Taylor for advice about n.m.r. experiments.

1. P. Hackett and G. Jaouen, Inorg. Chim. Acta., 12 (1975) L19; D. Sweigart and L.A.P. Kane-Maguire, J.C.S. Chem. Comm., (1976) 13; D. Sweigart, M. Gower and L.A.P. Kane-Maguire, J. Organometal. Chem., 108 (1976) C15; A. Salzer, Inorg. Chim. Acta., 17 (1976) 221 and 18 (1976) L31; A. Efraty, D. Liebman, J. Sikora and D.Z. Denney, Inorg. Chem., 15 (1976) 886; E. Efraty, S.S. Sandhu, B. Bystrek and D.Z. Denney, Inorg. Chem., 16 (1977) 2522.
2. M. Rosenblum, Acc.Chem.Res., 7 (1974) 122.
3. T.H. Whitesides, R.W. Arhart and R.W. Slaven, J. Amer. Chem. Soc., 95 (1973) 5792.
4. B.M. Trost and L. Webber, J. Amer. Chem. Soc., 97 (1975) 1611
5. H. tom Dieck and H. Friedel, J.C.S. Chem. Comm., (1969) 411.
6. N.A. Bailey, W.G. Kita, J.A. McCleverty, A.J. Murray, B.E. Mann and N.W. Walker, J.C.S. Chem. Comm., (1974) 592.
7. T.A. James and J.A. McCleverty, J. Chem. Soc., A (1971) 1596.

[†] All complexes reported herein analysed satisfactorily for C, H and N.