Journal of Organometallic Chemistry, 129 (1977) 175—179
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CATIONIC η^3-ALLYL-2,2′-BIPYRIDYLDICARBONYLMOLYBDENUM COMPLEXES: $[(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2L]^+ [BF_4]^-$

PAUL POWELL
The Bourne Laboratory, Department of Chemistry, Royal Holloway College, University of London, Egham Hill, Egham, Surrey TW 20 OEX (Great Britain)

(Received September 27th, 1976)

Summary

Several complexes $[(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2L]^+ [BF_4]^-$ (R = H or Me; L = NH_3, C_5H_5N, Ph_3P, Ph_3As, $(PhO)_3P$) have been prepared from $(\eta^3\text{-}C_3H_4R)$Mo(bipy)$(CO)_2Cl$ and $AgBF_4$ in acetone, followed by reaction with L. Their structures are discussed in the light of their infrared, ^1H and ^{13}C NMR spectra.

Introduction

There have been several reports of complexes of the general type $(\eta^3$-allyl)M(L—L)$(CO)_2X$ (M = Cr, Mo, W; L—L = a bidentate diimine ligand such as 2,2′-bipyridyl, 1,10-phenanthroline or an aliphatic diimine; X = halogen or pseudohalogen) [1—5]. Hull and Stiddard [3] obtained two salts $[\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2py]^+ [BF_4]^-$ (R = H, 2-Me) by heating $[(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2Cl]$ in acetone with pyridine in the presence of sodium tetrafluoroborate. In this paper a general method for the preparation of molybdenum complexes of the type $[(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2L]^+ [BF_4]^-$ is described. Very recently [5] Hsieh and West independently noted the formation of a similar ionic complex by the same method.

Results and discussion

Complexes Ia and Ib react rapidly with silver tetrafluoroborate in acetone to give silver chloride and a solution from which the acetone complex $[(\eta^3\text{-}C_3H_4R)$-Mo(bipy)$(CO)_2$acetone$]^+ [BF_4]^-$ can be isolated. Complexes IIc—IIe, IIIc—IIIf were obtained by adding this solution to an excess of the ligand L (L = Ph_3P, Ph_3As, $(PhO)_3P$ or C_5H_5N) dissolved in acetone. The salts were isolated by concentration of the resulting solution followed by precipitation with diethyl ether. The ammonia complexes IIb and IIIb were prepared by bubbling ammonia gas through a solution of IIa or IIIa respectively.

$$(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2Cl \xrightarrow[\text{acetone}]{AgBF_4} [(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2\text{acetone}]^+\ [BF_4]^-$$

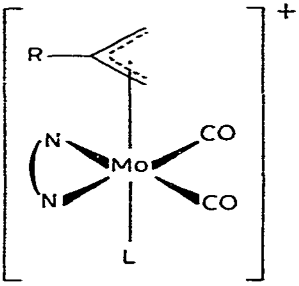
(Ia) R = H
(Ib) R = 2-Me

(IIa) R = H
(IIb) R = 2-Me

$$\xrightarrow[\text{acetone}]{L} [(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2L]^+\ [BF_4]^-$$

(IIb—IIf) R = H
(IIIb—IIIf) R = 2-Me

The complexes having L = NH_3 or C_5H_5N appear to be stable in air indefinitely both in the solid state and in solution, whereas solutions of those with L = Ph_3P, Ph_3As or $(PhO)_3P$ slowly decompose in air. The conductivities of methanol solutions of the salts are consistent with their formulation as 1 : 1 electrolytes (see Table 1 for analytical details and conductivities).



(IV)

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES $[(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2L]^+BF_4^-$

Compound	R	L	Colour	M.p. (°C)	Yield (%)	Found (calcd.) (%)			Λ^a
						C	H	Other	
IIb	H	NH_3	Maroon	209 (dec.)	57	39.66 (39.76)	3.64 (3.56)	N 9.21 (9.28)	97
IIc	H	C_5H_5N	Red	205 (dec.)	92	46.51 (46.63)	3.28 (3.52)		92
IId	H	Ph_3P	Brick red	160 (dec.)	60 [b]	56.56 (56.76)	4.17 (4.04)		92
IIe	H	Ph_3As	Ochre	180 (dec.)	60	53.40 (53.40)	4.00 (3.80)		
IIIa	CH_2	$(CH_3)_2CO$	Brown	158 (dec.)	76	44.65 (44.91)	4.30 (4.17)		
IIIc	CH_3	C_5H_5N	Deep red	182—186 (dec.)	91	47.99 (47.66)	4.04 (3.81)		91
IIId	CH_3	Ph_3P	Brown	165—170 (dec.)	84	57.61 (57.33)	4.51 (4.25)		86
IIIe	CH_3	Ph_3As	Brown	160 (dec.)	55	54.23 (54.06)	3.92 (4.00)		
IIIf	CH_3	$(PhO)_3P$	Brown	160 (dec.)	70	52.80 (53.71)	4.09 (3.98)		

[a] Equivalent conductivity (ohm^{-1}) in methanol at 25°C (10^{-3} *M* complex). Calc. for KCl at 10^{-3} *M*, 97 ohm^{-1} [13]. [b] Preparation done in CH_2Cl_2.

TABLE 2

^1H NMR CHEMICAL SHIFTS [a] (δ, ppm) FOR THE COMPLEXES $[(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2L]^+BF_4^-$

Compound	H_{syn}	H_{anti}	R	bipy	Other
IIb	3.46 [b]	1.57d J(HH) 9 Hz	3.3m	7.7—8.1m (2) 8.2—8.8m (4) 9.15d (2)	2.73(br) (NH_3)
IIc	3.73 [b]	1.88d J(HH) 9 Hz	3.5m	7.3—7.7m (2) 7.8—8.8m (9) 9.50d (2)	includes pyridine
IId	3.81 [b]	2.25d J(HH) 10 Hz	3.5m	7.4—7.7m (17) 8.0—8.6m (4) 8.86d (2)	includes Ph_3P
IIe	3.79 [b]	2.17d J(HH) 10 Hz	3.5m	7.3—7.8m (17) 8.2—8.6m (4) 8.95d (2)	includes Ph_3As
IIIa	3.45s	1.53s	1.21s	7.8—8.2m (2) 8.3—8.8m (4) 9.45d (2)	2.20s $(CH_3)_2CO$
IIIb	3.19s	1.52s	1.03s	7.7—8.1m (2) 8.3—8.8m (4) 9.17d (2)	2.53(br) (NH_3)
IIIc	3.55s	1.84s	1.19s	7.3—7.6m (2) 7.7—8.3m (4) 9.51d (2)	8.5 (5) (C_5H_5N)
IIId	3.45s	2.15s	0.90s	7.3—7.7m (17) 8.1—8.5m (4) 8.82d (2)	includes Ph_3P
IIIe	3.41s	2.17s	0.89s	7.2—7.9m (17) 8.1—8.5m (4) 8.98d (2)	includes Ph_3As
IIIf	3.62d J(PH) 2 Hz	2.29s	1.00d J(PH) 2 Hz	6.8—8.9m (23)	includes $(PhO)_3P$

[a] At 60 MHz in CD_3NO_2. [b] Resonance appears as a very distorted doublet.

The infrared spectra of all the compounds II and III show two bands of approximately equal intensity at ca. 1965 and 1875 cm^{-1}. This intensity pattern indicates a *cis*-arrangement of the two carbonyl ligands [5,6]. An X-ray crystallographic study of IIc has shown that the cation has the configuration IV [7]. The ^1H and ^{13}C NMR spectra of the salts (Tables 2 and 3) also indicate symmetrically bonded η^3-allyl groups, consistent with this structure in solution.

There have been rather few reports of ^{13}C NMR spectra for η^3-allyl complexes of transition elements, excepting palladium [8,9]. ^{13}C chemical shifts for five of the complexes are given in Table 3. The resonances of the bipyridyl ligand are assigned following Tänzer et al. [10], and of pyridine after Bancroft [11].

Experimental

All reactions were carried out in an atmosphere of oxygen-free nitrogen. The chloro complexes Ia and Ib were prepared from $Mo(bipy)(CO)_4$ [12] by the method of Hull and Stiddard [3].

Preparation of $[(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2L]^+[BF_4]^-$

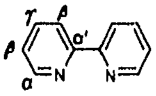
Silver tetrafluoroborate (0.4 g, 2 mmol) was added to a suspension of the

TABLE 3

^{13}C NMR CHEMICAL SHIFTS[a] FOR THE COMPLEXES

Compound	Allyl			Bipyridyl[b]				L		CO
	C_1C_3	C_2	CH_3	C_α	$C_{\alpha'}$	C_β	C_γ			
IIb	59,1	74,2		154,4	155,2	128,4 124,9	141,7			226,4
IIc	60,8	74,6		154,0	155,2	127,1 124,8	141,8	151,2 140,3 129,1	$C_{2,6}$ C_4 $C_{3,5}$	225,6
IIIa	57,4	85,1	19,2	154,0	155,3	128,4 124,8	142,0	19,2 $(CH_3)_2CO$		226,4
IIIc	58,8	86,2	19,2	153,8	155,1	127,1 125,0	142,0	151,1 140,2 129,1	$C_{2,6}$ C_4 $C_{3,5}$	226,0
IIIf	64,1	94,9d (J(PC) 7 Hz)	17,8	154,6	155,7	128,5 125,2	141,6	151,8d (J(PC) 12 Hz) 131,5 127,1 121,4d (J(PC) 4 Hz)	C_1 C_3 C_4 C_2	222,3

[a] In ppm relative to TMS (CD_3NO_2 solution). [b]



chloro complex Ia or Ib (2 mmol) in acetone (40 ml) with stirring. After 10 min the mixture was filtered into a solution of the appropriate ligand (3—4 mmol) in acetone (10 ml). If excess ligand is not used, the product tends to be contaminated with the acetone complex, particularly where L = Ph_3As or $(PhO)_3P$. After 30 min stirring the solvent was evaporated under reduced pressure to about 10 ml and the complex precipitated by addition of diethyl ether (ca. 50 ml). Analytical data are given in Table 1.

Preparation of $[(\eta^3\text{-}C_3H_4R)Mo(bipy)(CO)_2NH_3]^+ [BF_4]^-$

The procedure was similar to that described above, except that gaseous ammonia was bubbled through the solution after filtration of AgCl for about 10 min. The products were isolated in the same way and recrystallised from acetone/ether.

^1H NMR spectra were measured in CD_3NO_2 at 60 MHz on a Varian EM360 spectrometer. ^{13}C NMR spectra were obtained at PCMU, Harwell.

Acknowledgements

I thank the SRC for support. I am grateful to Mr. L.J. Russell for the conductivity measurements.

References

1 B.J. Brisdon and G.F. Griffin, J. Organometal. Chem., 76 (1974) C47.
2 H.D. Murdoch and R. Henzi, J. Organometal. Chem., 5 (1966) 552.
3 C.G. Hull and M.H.B. Stiddard, J. Organometal. Chem., 9 (1967) 519.
4 A.T.T. Hsieh and B.O. West, J. Organometal. Chem., 78 (1974) C40.
5 A.T.T. Hsieh and B.O. West, J. Organometal. Chem., 112 (1976) 285.
6 H. Schaper and H. Behrens, J. Organometal. Chem., 113 (1976) 361.
7 A.J. Graham and R.H. Fenn, J. Organometal. Chem., 37 (1972) 137.
8 M.H. Chisholm and S. Godelski in S.J. Lippard (Ed.), Progress in Inorganic Chemistry, Interscience, New York, Vol. 20, 1976 p. 299.
9 B.E. Mann, Adv. Organometal. Chem. 12 (1974) 135.
10 C. Tänzer, R. Price, E. Breitmaier, G. Jung and W. Voelter, Angew. Chem. Int. Ed., 9 (1970) 963.
11 G.M. Bancroft, K.D. Butler, L.E. Manzer, A. Shaver and J.E.H. Ward, Can. J. Chem., 52 (1974) 782.
12 M.H.B. Stiddard, J. Chem. Soc., (1962) 4713.
13 R.G. Hayter, J. Amer. Chem. Soc., 84 (1962) 3046.