Journal of Organometallic Chemistry, 78 (1974) C40—C42

Preliminary communication

η-ALLYL-MOLYBDENUM AND -TUNGSTEN CARBONYL COMPLEXES CONTAINING ALIPHATIC α-DIIMINES AS LIGANDS AND THEIR SOLVENT DEPENDENT INFRARED AND ELECTRONIC SPECTRA

A.T.T. HSIEH and B.O. WEST
Department of Chemistry, Monash University, Clayton, Victoria 3168 (Australia)

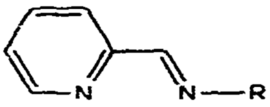
(Received July 22nd, 1974)

Summary

Pronounced solvent dependence is observed in the infrared and electronic spectra of the new η-allyl complexes (η-R$'C_3H_4$)M(CO)$_2$L$_2$X (M = Mo or W; R$'$ = H or Me; X = Cl, Br, I or NCS; L$_2$ = 1,2-ethanediylidenediimines or 2-pyridinaldimines).

Closely akin to the well-known heterocyclic ligands, 2,2$'$-bipyridyl and 1,10-phenanthroline [1,2], are the aliphatic α-diimines such as the *N,N'*-disubstituted 1,2-ethane diylidenediimines (I) and the related *N*-substituted 2-pyridinaldimines (II) which have not been investigated in detail [2]. These ligands are thought to have similar donor properties as the heterocyclic ligands apart from having comparable ligand field strengths [3]. However, there is evidence described herein and elsewhere [4—6] that the aliphatic α-diimine ligands (I) may be responsible for the difference in behaviour in their metal complexes as compared with those containing 2,2$'$-bipyridyl or 1,10-phenanthroline.

(I)



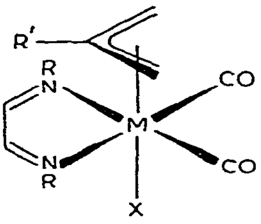
(II)

In order to investigate the electronic and solvent effects of the α-diimine substituents on the carbonyl groups *trans* to it*, we have prepared the new complexes (η-R$'C_3H_4$)M(CO)$_2$(RN=CHCH=NR)X (III) and (η-R$'C_3H_4$)M(CO)$_2$-

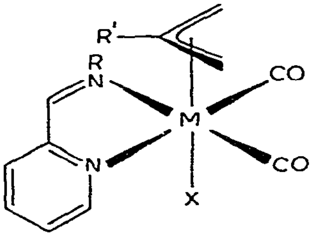
---

*The effects of carbonyl groups *cis* to the α-diimine ligand in the complexes $L_2Mo(CO)_4$ have have been shown [7] to be virtually independent of the nature of the solvent.

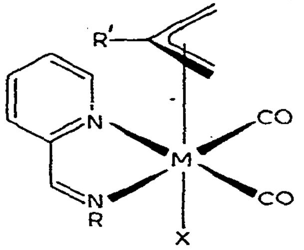
$(C_5H_4NCH{=}NR)X$ (IV) (M = Mo or W; R′ = H or Me, Et, i-Pr, t-Bu, Ph, cyclo-C_6H_{11}, *p*-MeC_6H_4, *p*-$MeOC_6H_4$ or 2,4-$Me_2C_6H_3$; X = Cl, Br, I or NCS) in good yields according to eqn. 1.



(III)



(IVa)



(IVb)

$$(\eta\text{-}R'C_3H_4)M(CO)_2(MeCN)_2X + L_2 \rightarrow (\eta\text{-}R'C_3H_4)M(CO)_2L_2X + 2\,MeCN \quad (1)$$

The α-diimine complexes (III), however, could not be obtained in any significant yield by the oxidative elimination reaction 2, which has been successfully

$$L_2M(CO)_4 + R'C_3H_4X \rightarrow (\eta\text{-}R'C_6H_4)M(CO)_2L_2X + 2CO \quad (2)$$

employed in the preparation of the 2,2′-bipyridyl, the 1,10-phenanthroline [8–10] and the 2-pyridinaldimine analogues. This difference in reactivity may be attributed to the larger steric hindrance imposed by the more bulky substituents on the nitrogen atoms in the α-diimine ligands.

These reasonably air-stable complexes III and IV which are non-electrolytes and monomeric in acetone, have been characterized by elemental analyses, mass spectrometry and chemical reactions and for the more soluble, by ^1H NMR spectroscopy. These results together with the presence of two almost equally intense carbonyl stretching absorptions suggest a *cis*-dicarbonyl structure. The recently determined crystal structures of the related 2,2′-bipyridyl and 1,10-phenanthroline complexes [10] lend further support to this configuration and to the contention that the η-allyl group is oriented as shown in III. It is noteworthy that each of the 2-pyridinaldimine complexes is isolated as a racemic mixture of the enantiomeric pair IVa and IVb.

The salient features in the electronic spectra of the complexes are the very intense $\pi\rightarrow\pi^*$ α-diimine ligand charge transfer band [4,6] in the $\lambda_{max} \sim 240$ nm region and the strong absorption ($\lambda_{max} > 550$ nm) attributable to the metal to ligand charge transfer [7]. The lower energy absorption which is also sensitive to the substituent(s) R on the nitrogen atom(s), undergoes a hypsochromic shift with the more polar solvents.

Chemical [11] and ^1H and ^{13}C NMR spectroscopic studies [12–14] have demonstrated that there is considerable π-delocalization within the five membered chelate ring which would almost certainly involve the filled d_π orbitals of the metal. As a consequence, any electronic perturbation, by solvent or through the substituent(s) on the nitrogen atom(s), would be felt by the carbonyl groups *trans* to the α-diimine ligand. Indeed, solvent dependent shifts are noted in the infrared spectra of the complexes; the two ν(CO) absorptions are being shifted to higher wave numbers with the less polar solvents.

Similar effects on the carbonyl groups *trans* to the α-diimine ligand L_2 have been observed in other carbonyl complexes such as $L_2Mo(CO)_4$, *fac*-$L_2Mo(CO)_3PPh_3$ and $L_2Mo(CO)_2(PPh_3)_2$ [7], and $XM(CO)_3L_2$ (M = Mn or Re; X = Cl, Br or I) [15].

Acknowledgement

We are grateful to the Australian Research Grants Committee for financial support.

References

1 W.R. McWhinnie and J.D. Miller, Advan. Inorg. Chem. Radiochem., 12 (1969) 135.
2 L.F. Lindoy and S.E. Livingstone, Coord. Chem. Rev., 2 (1967) 173.
3 M.A. Robinson, J.D. Curry and D.H. Busch, Inorg. Chem., 2 (1963) 1178.
4 H. tom Dieck and I.W. Renk, Chem. Ber., 104 (1971) 92.
5 R.C. Stouffer, D.W. Smith, E.A. Clevenger and T.E. Norris, Inorg. Chem., 5 (1966) 1167.
6 H. Bock and H. tom Dieck, Chem. Ber., 100 (1967) 228.
7 H. tom Dieck and I.W. Renk, Angew. Chem. Int. Ed. Engl., 9 (1970) 793.
8 C.G. Hull and M.H.B. Stiddard, J. Organometal. Chem., 9 (1967) 519 and ref. therein.
9 H. tom Dieck and H. Friedel, J. Organometal. Chem., 12 (1968) 173; 14 (1968) 375.
10 A.J. Graham and R.H. Fenn, J. Organometal. Chem., 17 (1969) 405; 25 (1970) 173; 37 (1972) 137.
11 E. Bayer, Angew. Chem., 73 (1961) 533.
12 E. Bayer, E. Breitmaier and V. Schurig, Chem. Ber., 101 (1968) 1594
13 C. Tänzer, R. Price, E. Breitmaier, G. Jung and W. Voelter, Angew. Chem. Int. Ed. Engl., 9 (1970) 963.
14 A.T.T. Hsieh and B.O. West, unpublished results.
15 A.T.T. Hsieh and B.O. West, to be published.