Journal of Organometallic Chemistry, 117 (1976) C111—C112

Preliminary communication

N,N′-DIARYLFORMAMIDINATO COMPLEXES OF THE PLATINUM GROUP METALS

STEPHEN D. ROBINSON* and ARVIND SAHAJPAL
Department of Chemistry, King's College, Strand, London WC2R 2LS (Great Britain)
(Received June 24th, 1976)

Summary

Some platinum group metal hydrides react with *N,N′*-diarylcarbodiimides in boiling toluene to yield products containing novel bidentate *N,N′*-diarylformamidinate (ArN—CH—NAr) ligands.

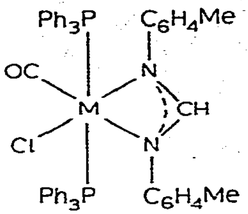
The importance of carboxylato and π-allylic complexes of the platinum metals in homogeneous catalysis [1] has stimulated interest in the chemistry and structure of related complexes containing analogous nitrogen and/or sulphur donor ligands including dithioformate [2] *N*-aryl- or *N*-alkyl-thioformamide [3] and 1,3-diaryltriazenide groups [4]. We now find that complexes containing the closely related, bidentate *N,N′*-diarylformamidinate (ArN═CH═NAr) ligands are conveniently prepared by treating platinum metal hydrides with *N,N′*-diarylcarbodiimides (A :N═C═NAr) in boiling toluene. Moreover, we find that the proton NMR spectra of the *N,N′*-di-*p*-tolylformamidinate ligands permit unambiguous assignment of ligand geometry and complex stereochemistry.

Thus the complexes [MCl(CO)(*p*-MeC_6H_4N═CH═NC_6H_4Me-*p*)$(PPh_3)_2$] (M = Ru or Os), obtained from the corresponding hydrides [MHCl(CO)$(PPh_3)_3$], have the stereochemistry I [M = Ru, τ(N═CH═N) 2.26(t), ^4J(PH) 2.7 Hz, τ(Me) 7.78 and 7.84; M = Os, τ(N═CH═N) 1.39(t), ^4J(PH) 2.5 Hz, τ(Me) 7.8 and 7.84]. Likewise the products obtained on treating the hydrides [MH_2(CO)$(PPh_3)_3$], [$RuH_2(PPh_3)_4$] or [$OsH_4(PPh_3)_3$], [$IrHCl_2(PPh_3)_3$] (*trans*-chlorides) and *mer*-[$IrH_3(PPh_3)_3$] with *N,N′*-di-*p*-tolylcarbodiimide are assigned structures II, III, IV and V respectively on the basis of ^{1}H NMR data (see Table 1)**. The magnetic equivalence of the methyl groups in the complexes IV and V establishes the symmetrical nature of the chelate (ArN═CH═NAr$^-$) ligands; therefore the non-equivalence of the methyl

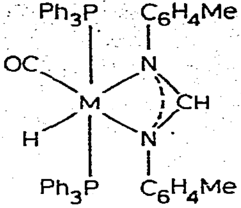
---

[*] To whom correspondence should be addressed.

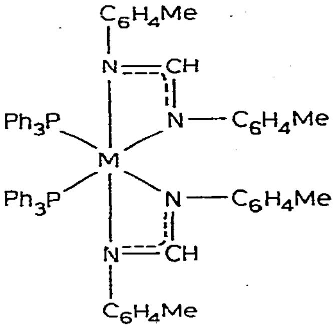
[**] All the products were obtained as analytically pure, air-stable, crystalline solids.



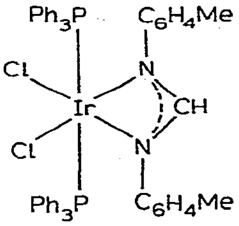
(I)



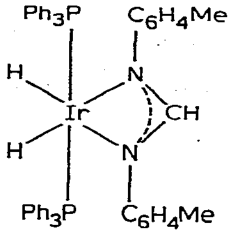
(II)



(III)



(IV)



(V)

TABLE 1

SPECTROSCOPIC DATA FOR *N,N'*-DI-*p*-TOLYLFORMAMIDINATO COMPLEXES[a]

Complex	τ(CH)[b]	^4J(PH) (Hz)	τ(CH_3)	τ(MH)[b]	^2J(PH) (Hz)
I (M = Ru)	2.26 (t)	2.65	7.78, 784	—	—
(M = Os)	1.39 (t)	2.5	7.80, 7.84	—	—
II (M = Ru)	masked	—	7.74, 7.90	23.37 (t)	20
(M = Os)	1.38 (br)	—	7.74, 7.90	24.58 (t)	17.3
III (M = Ru)	1.85 (br)	—	7.82, 7.90		
(M = Os)	0.76 (br)	—	7.79, 7.84		
IV	0.68 (t)	1.75	7.85		
V	0.97 (br)	—	7.85	32.76 (t)	17

[a] All complexes show IR bands at ca 1540, 1510, 1280, 1270, 920 and 820 cm^{-1} attributable to chelate *N,N'*-di-*p*-tolylformamidinate ligands. [b] t = triplet, br = broad envelope.

groups in the complexes I—III must reflect the differing nature of the groups *trans* to opposite ends of the (ArN=CH=NAr$^-$) ligands in these species. The chemistry of the coordinated *N,N'*-diarylformamidinate ligand is now being investigated.

References

1 R.F. Heck, Organotransition Metal Chemistry - a Mechanistic Approach, Academic Press, New York, 1974.
2 S.D. Robinson and A. Sahajpal, J. Organometal. Chem., 99 (1975) C63.
3 S.D. Robinson and A. Sahajpal, J. Organometal. Chem., 111 (1976) C26.
4 K.R. Laing, S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton, (1974) 1205.