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Preliminary communication

COORDINATION AND FRAGMENTATION OF p-TOLYLISOCYANATE BY PLATINUM METAL HYDRIDE COMPLEXES

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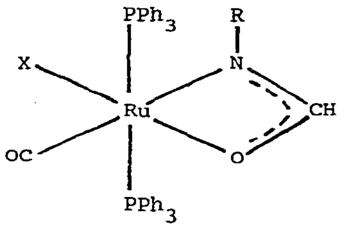
Summary   p-Tolyl*iso*cyanate (RNCO) undergoes coordination and fragmentation reactions with $[MHX(CO)(PPh_3)_3]$ (M = Ru or Os; X = Cl or Br), $[MH_2(CO)(PPh_3)_3]$ and $[RuH_2(PPh_3)_4]$ or $[OsH_4(PPh_3)_3]$ to yield products containing formamido ($RN \cdots CH \cdots O$), ureylene $[RN—C(O)—NR]$ and formamidinato ($RN \cdots CH \cdots NR$) ligands respectively.

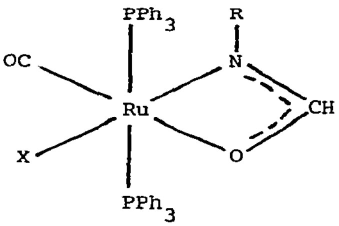
Current interest in the coordination chemistry of heteroallenes[1-5] prompts this report of our work on some novel reactions involving coordination and fragmentation of p-tolyl*iso*cyanate by platinum metal hydrides.

p-Tolyl*iso*cyanate reacts with the complexes $[MHX(CO)(PPh_3)_3]$ in boiling toluene over a period of *ca* 6 h (M = Ru, X = Cl or Br) or in boiling ethylbenzene over a period of *ca* 10 h (M = Os, X = Br) to yield formamido complexes $[MX(RN \cdots CH \cdots O)(CO)(PPh_3)_2]$ analogous to the thioformamido derivatives previously obtained from aryl*iso*thiocyanates (ArNCS) by a similar route[4].

The ruthenium complexes have stereochemistry (Ia or b) (^{31}P n.m.r. singlet δ 33-34†), whereas the osmium product in a mixture of several isomers (^{31}P n.m.r. singlet plus several AB patterns).

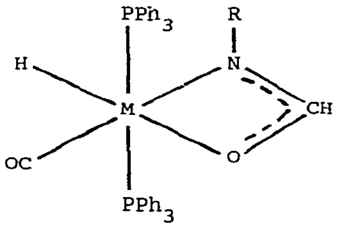


(Ia)

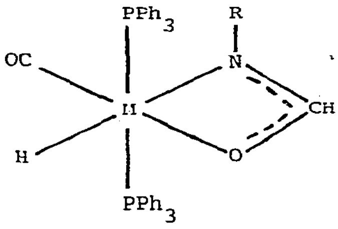


(Ib)

Under relatively mild conditions (M = Ru, benzene 15 min reflux; M = Os, toluene 8h. reflux) the complexes $[\mathrm{MH_2(CO)(PPh_3)_3}]$ also afford formamido derivatives $[\mathrm{MH(RN{\cdots}CH{\cdots}O)(CO)(PPh_3)_2}]$ which can be assigned stereochemistry (IIa or b) on the evidence of their n.m.r. spectra [M = Ru, τ_{MH} 26.5(t), ^2J(PH) 20.5 Hz; M = Os, τ_{MH} 23.2(t), ^2J(PH) 18.75 Hz.]



(IIa)



(IIb)

However, under more vigorous and/or prolonged reaction conditions (M = Ru, toluene 5h. reflux; M = Os, toluene 24h. reflux), cleavage of a molecule of isocyanate leading to formation of the ureylene complexes $[\mathrm{M\{RN{-}C(O){-}NR\}(CO)_2(PPh_3)_2}]$ occurs. The presence of the ureylene ligand in these products is confirmed by infrared spectroscopy [$\nu(\gt C = O)$ ca 1610 cm^{-1}], and the overall stereochemistry (III) is established by infrared and n.m.r. spectroscopic data [M = Ru, ν(CO) ca 1950 and 2020 cm^{-1}, τ_{Me} 7.8 singlet,

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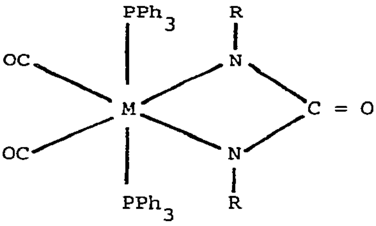
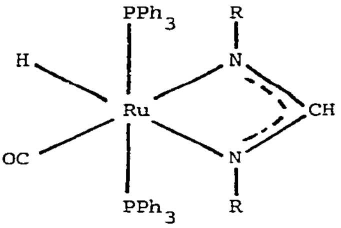
† ^{31}P n.m.r. chemical shifts referenced to 85% H_3PO_4.

δ_{PPh_3} 27.05 singlet; M = Os, ν(CO) <u>ca</u> 1930 and 2000 cm^{-1}, τ_{Me} 7.8 singlet, δ_{PPh_3} -0.44 singlet.†] Related ureylene complexes of rhodium, palladium and platinum have previously been obtained by fragmentation of <u>p</u>-tolylsulphonylisocyanate [6]. In the present work the low affinity for oxygen donor ligands relative to carbonyl groups displayed by ruthenium(II) and osmium(II) is probably a contributory factor promoting the fragmentation process.

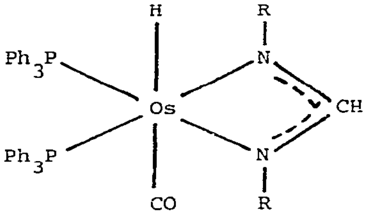


(III)

Finally, treatment of $[\mathrm{RuH_2(PPh_3)_4}]$ and $[\mathrm{OsH_4(PPh_3)_3}]$ with <u>p</u>-tolylisocyanate affords the formamidinato complexes $[\mathrm{MH(RN{\cdots}CH{\cdots}NR)(CO)(PPh_3)_2}]$ (M = Ru and Os respectively). The ruthenium complex is identical with an authentic specimen previously prepared from di-p-tolylcarbodiimide and shown by X-ray diffraction methods to possess stereochemistry (IVa) [5]. In contrast the less labile osmium product retains the intermediate stereochemistry (IVb) under the reaction conditions employed.



(IVa)



(IVb)

Spectroscopic data [M = Ru, τ_{MH} 23.37(t), $^2J(PH)$ 20 Hz, τ_{Me} 7.74 and 7.90; M = Os, τ_{MH} 20.54(t), $^2J(PH)$ 12.8 Hz; τ_{Me} 7.83] are in accord with these stereochemical assignments. Formation of the formamidinato ligands appears to involve fragmentation of two isocyanate moieties with concomitant formation of a carbonyl ligand and an oxygen atom, the latter being trapped as phosphine oxide. Again the affinity of the metal complex and the excess phosphine for the carbonyl and oxygen fragments respectively presumably contribute to the thermodynamic feasibility of the reaction observed.

REFERENCES

1. M.E. VOL'PIN, PURE AND APPLIED CHEMISTRY, 30 (1972) 607; M.E. VOL'PIN and I.S. KOLOMNIKOV, PURE AND APPLIED CHEMISTRY, 33 (1973) 567.
2. I.S. BUTLER and A.E. FENSTER, J. ORGANOMETALLIC CHEM., 66 (1974) 161.
3. S.D. ROBINSON and A. SAHAJPAL, INORG. CHEM., 16 (1977) 2718, see also INORG. CHEM., 17 (1978) 2340.
4. S.D. ROBINSON and A. SAHAJPAL, INORG. CHEM., 16 (1977) 2722.
5. L.D. BROWN, S.D. ROBINSON, A. SAHAJPAL and J.A. IBERS, INORG. CHEM., 16 (1977) 2728.
6. W. BECK, W. RIEBER, S. CENINI, F. PORTA and G. LaMONICA, J.C.S. DALTON, (1974) 298.