Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Cationic nitrosyl complexes of the type $[M(CO)_2NO(PPh_3)_2]^+$ $(M = Fe, Ru, or Os)$

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(Received August 2nd, 1971)

The reactivity of the coordinated nitric oxide group has recently received considerable attention[1]. Our interest in this subject led us to prepare a series of cationic nitrosyl complexes of general formula $[M(CO)_2NO(PPh_3)_2]^+$ (I, M = Fe; II, M = Ru; III, M = Os). Cation (I) has been reported previously[2] but was prepared in only moderate yields from *trans*-$Fe(CO)_3(PPh_3)_2$ (IV) and NOX (X = Cl, Br or NO_3).

We obtained (I) in quantitative yield from (IV) and NOY ($Y = BF_4$ or PF_6) in methanol–benzene. In contrast, when a solution of *trans*-$M(CO)_3(PPh_3)_2$ (V, M = Ru; VI, M = Os) in the same solvent was treated with NOY at ambient temperature the protonated species $[HM(CO)_3(PPh_3)_2]^+$ was formed[3]. This reaction must involve the initial formation of HPF_6.

$$NOPF_6 + MeOH \rightarrow HPF_6 + MeONO$$

The ready formation of these hydrido cations is in accord with the improved basic character of the *trans*-$M(CO)_3(PPh_3)_2$ complexes (M = Ru, Os). The protonated species were also obtained as stable salts by treatment of complexes (V) and (VI) with strong acids HX ($X = PF_6$, ClO_4, BF_4) in ether.

Treatment of $Ru_3(CO)_9(PPh_3)_3$ with NO^+ in methanol was found to cause metal–metal bond cleavage; a result which is also found in reaction with the iso-electronic species carbon monoxide. However migration of PPh_3 also occurs, resulting in the product $[Ru(CO)_2NO(PPh_3)_2]PF_6$ which is obtained from dichloromethane/ether as off-white needles. Similar treatment of $Os_3(CO)_9(PPh_3)_3$ did not result in the formation of (III). However, the labile chloride in $Os(CO)(NO)(PPh_3)_2Cl$ may be displaced by carbon monoxide in the presence of $NaBPh_4$, affording the required cation (III) in high yield as the tetraphenylborate salt. Cation (II) was also produced by a similar route. The characterisation of (I), (II) and (III) followed directly from analytical and spectroscopic data (Table 1).

Certain differences in reactivity between the three cations have been noted. When a suspension of (I) or (III) in methanol was treated with methoxide ion the

TABLE 1

INFRARED DATA [a] (cm^{-1})

	ν(CO)	ν(NO)
$[Fe(CO)_2(NO)(PPh_3)_2]PF_6$	2051s, 1995vs	1792vs
$[Ru(CO)_2(NO)(PPh_3)_2]PF_6$	2065s, 2014vs	1765vs
$[Ru(CO)_2(NO)(PPh_3)_2]BPh_4$		
$[Os(CO)_2(NO)(PPh_3)_2]BPh_4$	2055s, 1998vs	1748vs
$[RuH(CO)_3(PPh_3)_2]PF_6$ [b]	2127m, 2077s, 2057vs	
$Fe(CO)(NO)(PPh_3)_2CO_2Me$ [b]	1915vs	1693vs
$Os(CO)(NO)(PPh_3)_2CO_2Me$ [b]	1911vs	1648vs

[a] CH_2Cl_2 solution unless stated otherwise. [b] Nujol mull. ν(CO) [carboxyl] 1605 cm^{-1}(Fe), 1617 cm^{-1} ($CHCl_3$ solution.

carboxyl derivatives $M(CO)(NO)(PPh_3)_2CO_2Me$ (M = Fe or Os) were formed whereas the reaction of (II) is complex and does not lead to a stable derivative★. The cations (I) and (III) were reformed in almost quantitative yield as the stable PF_6^- salt by treating the carboxyl derivatives with HPF_6 in methanol. Both (II) and (III) react rapidly with chloroform under reflux and nitrogen to give a mixture of $M(NO)(PPh_3)_2Cl_3$ and *cis*-$M(CO)_2(PPh_3)_2Cl_2$ but (I) is comparatively stable under these conditions. In air, however, (III) reacts differently to produce $Os(NO)(PPh_3)_2(CO_3)Cl$[5] and *cis*-$Os(CO)_2(PPh_3)_2Cl_2$. With chlorine (II) is immediately oxidised to $Ru(NO)(PPh_3)_2Cl_3$ whereas (III) gives *cis*-$Os(CO)_2(PPh_3)_2Cl_2$ reflecting the relative metal–nitrogen and metal–carbon bond strengths in each case. Indeed the IR data does suggest a weaker bonding of metal to carbonyl in the case of cation (II) as compared with (I) and (III).

We thank the Science Research Council and ICI, HOC Division for financial support and Johnson Matthey Co. Ltd. for the loan of ruthenium and osmium salts.

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★The authors wish to thank F.P. Stefanini and M.J. Mays for personal communication of their work in this area.