Journal of Organometallic Chemistry, 363 (1989) 371–376
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09576

Coordinative activation of nitrosoarenes: synthesis and protonation of the osmaoxaziridine $[OsCl(NO)(ONC_6H_5)(PPh_3)_2]$

Max Herberhold

Laboratorium für Anorganische Chemie der Universität Bayreuth, Universitätsstraße 30, D-8580 Bayreuth (F.R.G.)

and Anthony F. Hill

Department of Chemistry, University of Warwick, Coventry CV4 7AL (U.K.)

(Received August 9th, 1988)

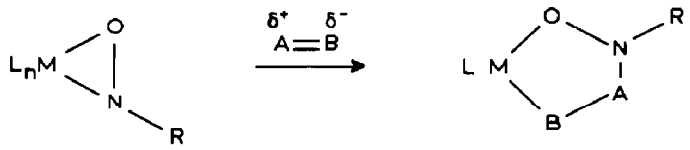
Abstract

Nitrosobenzene, reacts readily with $[OsCl(NO)(PPh_3)_2(L)]$ ($L = C_2H_4$, PPh_3) to replace the labile ligand, L, and form of complex $[OsCl(NO)(ONPh)(PPh_3)_2]$ in which the nitrosoarene ligand is coordinated through both nitrogen and oxygen. The nitrosobenzene complex reacts reversibly with hydrogen chloride to provide a 1/1 adduct, formulated as the divalent osmium hydroxylaminato complex $[OsCl_2\{N(OH)Ph\}(NO)(PPh_3)_2]$.

Introduction

The isolation of the complexes $[Pt(ONAr)(PPh_3)_2]$ (Ar = aryl), and subsequent reactivity studies with multiple-bond containing substrates [1–3] promise a diverse chemistry based on the coordinative activation of the N=O groups. The reactivity of coordinated nitrosoarenes is, however, not yet well understood. Some attempts to utilise nitrosoarenes as sources of an imino, or nitrene, fragment "Ar–N:" have been successful [4,5], but others less so [6]. The nitroso group of nitrosoalkanes and nitrosoarenes may ligate to a metal in a number of ways depending primarily on the nature of the metal centre involved [7,8]. The bidentate mode of coordination tends to be irreversible. Thus the complex $[Pt(ONPh)(PPh_3)_2]$ treated with a variety of potential ligands (alkynes, alkenes, carbon disulphide, nitrosonium ion etc.) leads to coupling reactions involving the nitrosoarene ligand and the added reagent, rather than simple substitution [1–3,7] (Scheme 1).

0022-328X/89/$03.50



Scheme 1. Coupling reactions of nitrosoarenes at low-valent metal centres. $L_nM = [(PPh_3)_2Pt]$. A=B = OC=O, SC=S, O=N$^+$, OC=NR, RC≡CR, $(NC)_2C=C(CN)_2$.

We describe here the synthesis of a novel nitrosobenzene complex of zerovalent osmium and report an important reaction of the complex viz. reversible protonation to give hydroxylaminato complex of divalent osmium.

Results and discussion

Synthesis and spectroscopic characterisation of [OsCl(NO)(ON-Ph)(PPh$_3$)$_2$]

The ruthenium complex [RuCl(NO)(ON-Ph)(PPh_3)$_2$] has been prepared by treatment of the reactive 16-electron complex fragment [RuCl(NO)(PPh_3)$_2$] with nitrosobenzene [3]. The complex was rather unstable and complete characterisation was not possible, although the identity of the compound was clear from elemental microanalysis and infrared data. We have found the osmium fragment [OsCl(NO)(PPh_3)$_2$] (analogous to [RuCl(NO)(PPh_3)$_2$]) very useful for the stabilisation of small reactive molecules [8–12]. Unlike the corresponding ruthenium complex [13], [OsCl(NO)(PPh_3)$_2$] is not available as the free complex [14]. The chemistry of this fragment has nevertheless been extensively investigated through the use of labile adducts [OsCl(NO)(PPh_3)$_2$(L)] (L = C_2H_4, PPh_3) [9–12,14,15]. With a view to obtaining model complexes which might be more amenable to study than the unstable ruthenium compounds, we have investigated the synthesis of the complex [OsCl(NO)(ON-Ph)(PPh_3)$_2$].

The tris(phosphine) complex [OsCl(NO)(PPh_3)$_3$] [9] reacts with 1–2 equivalents of nitrosobenzene to provide, as the major product (60–70%), an orange compound formulated as [OsCl(NO)(ONPh)(PPh_3)$_2$]. Unlike the ruthenium complex [RuCl(NO)(ONPh)(PPh_3)$_2$], the product is indefinitely stable in the solid state under air. A band in the infrared spectrum (Nujol) at 1729 cm^{-1} is assigned to the nitrosyl ligand and the frequency compares well with those for the related complexes [OsCl(NO)(O_2)(PPh_3)$_2$] (1740 [14]) and [OsCl(NO)(CH_2O)(PPh_3)$_2$] (1710 [14,15]), and [RuCl(NO)(ON-Ph)(PPh_3)$_2$] (1740 cm^{-1} [3]). A band at 958 cm^{-1} may be attributed predominately to the nitrogen-oxygen stretch of the π-bound nitrosoarene. This frequency may be compared with those in the complexes [Pt(ONC_6H_4Me-2)(PPh_3)$_2$] (975 cm^{-1} [3]) containing π-bound nitrosotoluene, and with the oxygen–oxygen stretching frequency for [OsCl(NO)(O_2)(PPh_3)$_2$] (840 cm^{-1} [14]), and contrasted with the position of the ν(NO)-associated band in the spectrum of [$PtCl_2$(ON-CMe_3)$_2$] (1555 cm^{-1} [8]), which contains a monodentate coordinated nitrosoalkane. The low value of ν(NO) supports the assumption of bidentate (N,O) coordination of the N–O moiety to osmium in [OsCl(NO)(ON-Ph)(PPh_3)$_2$].

The well-established reaction of phosphines with nitroso compounds leading to phosphine oxides and iminophosphoranes, i.e.:

$$2\ R_3P + O{=}N{-}R' \rightarrow R_3P{-}O + R_3P{-}N{-}R'$$

is presumably responsible for the moderate yields obtained after chromatographic purification of $[OsCl(NO)(ONPh)(PPh_3)_2]$. Indeed, the product itself, $[OsCl(NO)(ONPh)(PPh_3)_2]$ may be sensitive to the presence of excess of phosphine, as, for example, is the ruthenium analogue [3]. In an attempt to improve the synthesis, the reaction of the ethylene complex $[OsCl(NO)(C_2H_4)(PPh_3)_2]$ [14,15] with nitrosobenzene was investigated. Treatment of the ethylene complex with one equivalent of nitrosobenzene in tetrahydrofuran gives the desired complex $[OsCl(NO)(ONPh)(PPh_3)_2]$ in quantitative yield as indicated spectroscopically, and in 94% isolated yield.

$$[OsCl(NO)(C_2H_4)(PPh_3)_2] + O{=}N{-}Ph \rightarrow [OsCl(NO)(ON{-}Ph)(PPh_3)_2] + C_2H_4$$

Protonation of coordinated nitrosobenzene

The reactions of coordinated nitrosoarenes with electrophiles typically result in coordination of the electrophile to the nitrogen atom of the nitroso group, followed by metallacyclic ring closure [1–3] (Scheme 1). In contrast to these observations, the reactions of electrophiles with the isolobally related molecule formaldehyde when bound to low-valent osmium centres give products derived from electrophilic attack at the oxygen atom [16]. It was therefore of interest to investigate the ambidenticity of the nucleophilic nitrosoarene ligand in $[OsCl(NO)(ONPh)(PPh_3)_2]$. Treatment of a dichloromethane solution of the nitrosoarene complex with aqueous hydrochloric acid immediately gave an orange-brown complex, which was isolated following addition of ethanol and concentration of the solution under reduced pressure. Surprisingly, attempts to further purify this compound by column chromatography on silica gelled to complete recovery of the starting complex. Similarly, treatment of the protonated complex with the non-nucleophilic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), gave good yields of $[OsCl(NO)(ONPh\}(PPh_3)_2]$.

The infrared data support the formulation of the protonated product as the divalent hydroxylaminato-osmium complex $[OsCl_2\{N(OH)Ph\}(NO)(PPh_3)_2]$: the appearance of a band at 3243 cm^{-1} corresponds to a hydroxyl group rather than a metal hydride which would be expected to be apparent at ca. 2000 cm^{-1}. The ν(NO) stretching band observed at 958 cm^{-1} in the precursor complex is replaced by a band at 884 cm^{-1} in the protonated product. This is consistent with a formal reduction in the N–O bond order upon conversion of a π-bound nitroso group (which retains a degree of multiple bonding between N and O) to a hydroxylaminato ligand in which the bond order would more closely approach unity. Clearly in neither case are the N–O bond orders integral. At this point we can not exclude an alternative formulation in which protonation occurs at the nitrogen atom to give the complex "$[OsCl_2(ONHPh)(NO)(PPh_3)_2]$", but further arguments (vide supra) support the former formulation. Finally, the nitrosyl-associated band in the infrared moves upon protonation from 1729 to 1798 cm^{-1}. This value is typical of divalent osmium (cf. [17]) suggesting an oxidation of the osmium center $[Os^0 \rightarrow Os^{II}]$, whilst the appearance of two bands in the ν(OsCl) region of the far-infrared (319, 303 cm^{-1}) indicate the presence of two *cis*-disposed chloride ligands. Thus we describe the reaction by the equation:

$$[OsCl(NO)(ONPh)(PPh_3)_2] + HCl \rightarrow [OsCl_2\{N(OH)Ph\}(NO)(PPh_3)_2]$$

The protonation of $[Os(NO)_2(PPh_3)_2]$ by aqueous hydrochloric acid leads ultimately to $[OsCl_2\{N(OH)H\}(NO)(PPh_3)_2]$, and a reasonable intermediate proposed

for this reaction is $[OsCl(NO)(ONH)(PPh_3)_2]$ [18]. This formulation was further supported by the reaction of $[OsCl(NO)(CO)(PPh_3)_2]$ with HCl to provide a stable complex of "HN=O" [18] which was subsequently structurally characterised as $[OsCl_2\{N(=O)H\}(CO)(PPh_3)_2]$ [19] (Scheme 2).

$$L_jM\text{–}NO \xrightarrow{HCl} L_jMCl\{N(=O)H\}$$

$$L_kM\text{–}NO \xrightarrow{HCl} L_kMCl\{N(=O)H\} \xrightarrow{HCl} L_kMCl_2\{N(OH)H\}$$

$$L_nM(PPh_3)\text{–}NO \xrightarrow[-PPh_3]{HCl} L_nMCl\{N(=O)H\} \xrightarrow{HCl} L_nMCl_2\{N(OH)H\} \xrightarrow{HCl} L_nMCl_3\{N(OH)H_2\}$$

Scheme 2. Protonation of nitrosyl and nitrosyl hydride ligands [18]; $L_jM = [OsCl(CO)(PPh_3)_2]$; $L_kM = [Os(NO)(PPh_3)_2]$; $L_nM = [Ir(PPh_3)_2]$.

Thus $[OsCl(NO)(ON\text{-}Ph)(PPh_3)_2]$ corresponds to a derivative of the proposed intermediate $[OsCl(NO)(ON\text{-}H)(PPh_3)_2]$, which could not be isolated owing to the speed of proton transfer reactions at oxygen.

Experimental

General experimental procedures and instrumentation have been given elsewhere [11]. Nitrosobenzene was purchased (Fluka), and used without further purification. The compounds $[OsCl(NO)(PPh_3)_2(L)]$ ($L = PPh_3$ [9], C_2H_4 [15]) have been described previously.

$[OsCl(NO)(ON\text{-}Ph)(PPh_3)_2]$

(A): A suspension of $[OsCl(NO)(PPh_3)_3]$ (0.50 g, 0.48 mmol) and nitrosobenzene (0.11 g, 1.03 mmol) in toluene (20 cm^3) was stirred for ten minutes and solvent was then removed under reduced pressure. The residue was dissolved in a minimum of dichloromethane and chromatographed on silica gel, with dichloromethane as eluant. The bright orange band was collected and concentrated in vacuo, and ethanol was added to induce crystallisation of the orange complex. Yield 0.26–0.30 g (60–70%).

(B): A solution of $[OsCl(NO)(C_2H_4)(PPh_3)_2]$ (0.40 g, 0.50 mmol) and nitrosobenzene (0.055 g, 0.51 mmol) in tetrahydrofuran (20 cm^3) was stirred for five minutes, then ethanol (30 cm^3) was added and the solution was concentrated under reduced pressure. Additions of ethanol gave a precipitate of the bright orange complex, which was filtered off. Yield 0.42 g (94%) (spectroscopically quantitative). M.p. 121 °C (decomp.). Anal. Found: C, 57.17; O, 3.96; N, 4.07. $C_{42}H_{35}ClN_2O_2OsP_2$ calcd.: C, 57.04; O, 3.62; N, 3.17%.

$[OsCl_2\{N(OH)Ph\}(NO)(PPh_3)_2]$

A solution of $[OsCl(NO)(ONPh)(PPh_3)_2]$ (0.25 g, 0.27 mmol) in dichloromethane (20 cm^3) was treated with one drop of concentrated hydrochloric acid. The solution

Table 1

Spectroscopic characterisation

Compound	Infrared (Nujol) (cm^{-1})			NMR ($CDCl_3$) [a] δ(ppm)	
	ν(NO)	ν(OsCl)	other	^1H [b]	$^{31}P\{^1H\}$ [c]
$[OsCl(NO)(ON\text{-}Ph)(PPh_3)_2]$ (orange)	1729	297	1207 [ν(CN)] 958 [ν(NO)]		−6.02 −6.66 [d]
$[OsCl_2\{N(OH)Ph\}(NO)(PPh_3)_2]$ (orange-brown)	1798	319 303	3243 [ν(OH)] 884 [ν(NO)]	1.64[OH]	−14.9

[a] Data were obtained from saturated solutions of the complex in $CDCl_3$ at room temperature. [b] Data are reported relative to internal $\delta(SiMe_4) = 0.00$. [c] Data are reported relative to external $\delta(D_3PO_4) = 0.00$. [d] Outer pair and AB-quartet not observed.

was stirred rapidly for five minutes, then ethanol was added, and the solvent volume was reduced to ca. 10 cm^3 in vacuo (rotary evaporator) to induce crystallisation. The concentrated solution was cooled to −30 °C overnight and the product filtered off, washed with cold (0 °C) ethanol (5 cm^3), and dried in vacuo. Yield 0.18 g (69%). The complex decomposes without melting at 154 °C. It may be recrystallised from dichloromethane/ethanol mixtures in which a trace of hydrogen chloride gas has been dissolved. The complex crystallises with 0.25 mol of dichloromethane, as is evident from ^1H NMR integration and elemental microanalysis. Anal. Found: C, 53.75; H, 4.04; N, 3.03; Cl, 9.17. $C_{42}H_{36}Cl_2N_2O_2OsP_2 \cdot (0.25CH_2Cl_2)$ calcd.: C, 53.70; H, 4.11; N, 2.96; Cl, 9.38%.

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We also thank the Deutscher Akademischer Austauschdienst for a fellowship (to A.F.H.).

References

1 P.L. Bellon, S. Cenini, F. Demartin, M. Pizzotti and F. Porta, J. Chem. Soc., Chem. Commun., (1982) 265.
2 S. Cenini, F. Porta, M. Pizzotti and G. La Monica, J. Chem. Soc., Dalton Trans., (1984) 355.
3 C.J. Jones, J.A. McCleverty and A.S. Rothin, J. Chem. Soc., Dalton Trans., (1985) 401.
4 S.-H. Han, G.L. Geoffroy and A.L. Rheingold, Inorg. Chem., 26 (1987) 3426.
5 J.A. Smieija, J.E. Gozum and W.L. Gladfelter, Organometallics, 6 (1986) 1311.
6 G. Vasapollo, P. Giannoccaro, C.F. Nobile and F. Allegretta, J. Organomet. Chem., 270 (1984) 109.
7 (a) M. Pizzotti, F. Porta, S. Cenini, F. Demartin and N. Masciocchi, J. Organomet. Chem., 330 (1987) 265; (b) R.E. Little and R.J. Doedens, Inorg. Chem., 12 (1973) 537; (c) D. Mansuy, M. Dreme, J.C. Chottard and J. Guilhem, J. Organomet. Chem., 161 (1978) 207.
8 D.L. Packett, W.C. Trogler and A.L. Rheingold, Inorg. Chem., 26 (1987) 4308.
9 A.F. Hill, W.R. Roper, J.M. Waters and A.H. Wright, J. Am. Chem. Soc., 105 (1983) 5939.
10 M. Herberhold and A.F. Hill, J. Organomet. Chem., 309 (1986) C29.
11 M. Herberhold, A.F. Hill, N.M. McAuley and W.R. Roper, J. Organomet. Chem., 310 (1986) 95.
12 M. Herberhold and A.F. Hill, J. Chem. Soc., Dalton Trans., (1988) 2027.
13 (a) M.H.B. Stiddard and R.E. Townsend, Chem. Comm., (1969) 1372; (b) J. Reed, C.E. Pierpont and R. Eisenberg, Inorg. Synth., 16 (1976) 21.
14 A.H. Wright, Ph.D. thesis, University of Auckland, 1983.

15 W.R. Roper, J. Organomet. Chem., 300 (1986) 167.
16 G.R. Clark, C.E.L. Headford, K. Marsden and W.R. Roper, J. Organomet. Chem., 231 (1982) 335.
17 N.G. Connelly, Inorg. Chim. Acta Reviews, 6 (1972) 47.
18 K.R. Grundy, C.A. Reed and W.R. Roper, Chem. Commun., (1970) 1501.
19 R.D. Wilson and J.A. Ibers, Inorg. Chem., 18 (1979) 336.