Notes

Insertion of NO into Transition Metal–Aryl Bonds: Formation of Zirconium Complexes containing the $[ON(R)NO]^-$ (R = Ph or *p*-MeC_6H_4) Ligand

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Reaction of $[Zr(\eta\text{-}C_5H_5)_2Ph_2]$ with NO in benzene afforded $[Zr(\eta\text{-}C_5H_5)_2Ph\{ON(Ph)NO\}]$. Treatment of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with $Ag[ON(R)NO]$ (R = Ph or *p*-MeC_6H_4) gave $[Zr(\eta\text{-}C_5H_5)_2Cl\{ON(R)NO\}]$, whereas with $[NH_4][ON(C_6H_4Me\text{-}p)NO]$, only $[Zr\{ON(C_6H_4Me\text{-}p)NO\}_4]$ was formed.

Reaction of NO with d^0 and d^{10} transition metal–alkyls affords complexes containing the *N*-alkyl-*N*-nitrosohydroxylaminato-ligand, $[ON(R)NO]^-$.[1-3] Thus $[Zr(\eta\text{-}C_5H_5)_2Me_2]$ and $ZnMe_2$ were converted into $[Zr(\eta\text{-}C_5H_5)_2\{ON(Me)NO\}_2]$[4] and $[Zn\{ON(Me)NO\}_2]$,[5] respectively. It is also known that methyl group migration to NO can occur in such species as $[Co(\eta\text{-}C_5H_5)Me(NO)]$, affording complexes containing MeNO,[6] and that direct alkylation of transition metal-bonded NO can afford, presumably, alkylnitroso-intermediates which rearrange to more stable organo-nitrogen derivatives.[7,8]

It has not been clearly demonstrated, however, that transition metal-*aryl* complexes can undergo 'NO insertion' into the M–C(aryl) bond, and in this paper we describe the reactions of the 'model compound,' $[Zr(\eta\text{-}C_5H_5)_2Ph_2]$, with NO, and our attempts to characterise the product.

Results and Discussion

When NO was passed into a benzene solution of $[Zr(\eta\text{-}C_5H_5)_2Ph_2]$, the mixture became yellow and, on evaporation and work-up, a white solid was obtained. This solid was 'dried' *in vacuo* at 60—70 °C for at least 2 d, whereupon elemental analyses showed that only two moles of NO were taken up per mole of zirconium complex, the data being consistent with the formulation $[Zr(\eta\text{-}C_5H_5)_2Ph\{ON(Ph)NO\}]$.

I.r. spectroscopic data obtained from the new compound suggested that the chelated ON(Ph)NO ligand was present, the bands at 1 345, 1 295, 1 218, and 928 cm^{-1} (Table 1) being characteristic of the M{ON(R)NO} chelate ring.[9] The ^1H n.m.r. spectrum of $[Zn(\eta\text{-}C_5H_5)_2Ph\{ON(Ph)NO\}]$ in several solvents (Table 2) revealed a sharp singlet due to the $\eta\text{-}C_5H_5$ protons at δ *ca.* 5.9, which was relatively solvent independent (except in C_6D_6), and a broad multiplet due to the aryl protons, in the ratio 1 : 1, as expected.

In order to substantiate further the nature of $[Zr(\eta\text{-}C_5H_5)_2Ph\{ON(Ph)NO\}]$, we prepared the related chloro-complexes, $[Zr(\eta\text{-}C_5H_5)_2Cl\{ON(R)NO\}]$ (R = Ph or *p*-MeC_6H_4), by reacting $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ with $Ag[ON(R)NO]$. The i.r. spectra of these complexes were very similar to those of their phenyl analogues, especially in the regions characteristic of the ON(R)NO ligand, *viz. ca.* 1 350, *ca.* 1 300, *ca.* 1 210, and *ca.* 930 cm^{-1}. The ^1H n.m.r. spectra of the complexes were consistent with the presence of two C_5H_5 rings per ON(R)NO group (Table 2). Furthermore, we noted that the chemical shifts of the aryl protons, and of the methyl protons in *p*-MeC_6H_4, exhibited

Table 1. I.r. spectroscopic data obtained from zirconium complexes in KBr discs

Compound	Bands characteristic of $[ON(R)NO]^-$ (cm^{-1})
$[Zr(\eta\text{-}C_5H_5)_2Ph\{ON(Ph)NO\}]$	1 345s, 1 295vs, 1 218s, 928s
$[Zr(\eta\text{-}C_5H_5)_2Cl\{ON(C_6H_4Me\text{-}p)NO\}]$	1 350s, 1 298vs, 1 205s, 925s
$[Zr(\eta\text{-}C_5H_5)_2Cl\{ON(Ph)NO\}]$	1 362vs, 1 300vs, 1 215vs, 935vs
$[Zr\{ON(C_6H_4Me\text{-}p)NO\}_4]$	1 360s, 1 305vs, 1 215vs, 1 175vs, 945vs
$Ag[ON(Ph)NO]$	1 340vs, 1 275vs, 1 280s, 920s
$Ag[ON(C_6H_4Me\text{-}p)NO]$	1 335s, 1 275s, 1 230s, 920s

Table 2. ^1H N.m.r. spectra (δ/p.p.m., internal SiMe4 reference) for zirconium complexes

Complex	Solvent	$\delta(C_5H_5)$	$\delta(C_6H_5)$	$\delta(CH_3)$
$[Zr(\eta\text{-}C_5H_5)_2Ph\{ON(Ph)NO\}]$	C_6D_6	5.79	6.83—8.00[a]	
	$CDCl_3$	5.95	6.90—8.00[a]	
	CD_2Cl_2	5.95 (1)[b]	6.72—7.95 (1)[a,b]	
$[Zr(\eta\text{-}C_5H_5)_2Cl\{ON(Ph)NO\}]$	C_6D_6	5.98	6.68—8.02	
	$CDCl_3$	6.24 (2)[b]	7.78—8.04 (1)[b]	
	CD_2Cl_2	6.23	7.3—8.0	
	$(CD_3)_2CO$	6.28	7.38—8.14	
$[Zr(\eta\text{-}C_5H_5)_2Cl\{ON(C_6H_4Me\text{-}p)NO\}]$	C_6D_6	5.98	7.24[c]	1.88
	$CDCl_3$	6.24 (10)[b]	7.54 (4)[b,c]	2.42 (3)[b]
	CD_2Cl_2	6.20	7.50	2.39
	$(CD_3)_2CO$	6.24	7.54[c]	2.42
$[Zr(\eta\text{-}C_5H_5)_2Cl_2]$	CD_2Cl_2	6.48		
$[Zr(\eta\text{-}C_5H_5)_2Ph_2]$	CS_2	6.02	6.4—7.36	

[a] $Zr\text{–}C_6H_5 + ON(C_6H_5)NO$. [b] Relative area in parentheses. [c] A_2B_2 spectrum.

a marked solvent dependence. This phenomenon has also been observed in the δ values for the methyl protons in [Zr(η-C_5H_5)$_2$Me{ON(Me)NO}], prepared by reaction of NO with [Zr(η-C_5H_5)$_2Me_2$].[4]

When [Zr(η-C_5H_5)$_2Cl_2$] was treated with [NH_4][ON(C_6H_4Me-*p*)NO], however, complete displacement of the ligands at the metal occurred, and only [Zr{ON(C_6H_4Me-*p*)NO}$_4$] was isolated in spite of using less than four mol equivalents of the NH_4^+ salt. This species was also formed by direct reaction of $ZrCl_4$ with Ag[ON(C_6H_4Me-*p*)NO]. Cupferron {[NH_4][ON(Ph)NO]} has long been used as an analytical reagent for Zr and, although the composition of the zirconium 'cupferronates' is variable and dependent on reaction time, acidity, and method of preparation, [Zr{ON(Ph)NO}$_4$] has been isolated and characterised crystallographically.[10] The zirconium atom is eight-co-ordinate, the O atoms forming an irregular dodecahedron with triangular faces. We presume that [Zr{ON(C_6H_4Me-*p*)NO}$_4$] is similar.

Although we have not demonstrated conclusively that the ON(R)NO ligand in [Zr(η-C_5H_5)$_2$X{ON(R)NO}] (X = Ph or Cl) is bidentate, we feel that this is a reasonable supposition, especially in view of the structure of [Zr{ON(Ph)NO}$_4$]. Accordingly, the metal in [Zr(η-C_5H_5)$_2$Ph{ON(Ph)NO}] is formally nine-co-ordinate, assuming that the cyclopentadienyl rings each occupy three co-ordination sites. The inertness of the second Zr–Ph bond towards NO 'insertion' may therefore be understood in terms of the inability or unwillingness of the metal to increase its co-ordination number further. A similar situation has been apparently encountered in [WMe_4{ON(Me)NO}$_2$], which is eight-co-ordinate, and where further NO 'insertion' into W–Me bonds, which would require an increase in co-ordination number, does not occur.[2]

From the results reported here, we conclude that 'insertion' of NO into d^0 and d^{10} metal-aryl complexes will probably occur in a manner entirely similar to that of their alkyl analogues.

Experimental

Cupferron, [NH_4][ON(Ph)NO], and [NH_4][ON(C_6H_4Me-*p*)NO] were prepared as described in the literature.[11] Ag[ON(R)NO] (R = Ph or *p*-MeC_6H_4) has been reported earlier[12] and [Zr(η-C_5H_5)$_2Cl_2$] and $ZrCl_4$ were supplied by Aldrich Chemical Co. Ltd. NO gas was prepared by reaction of $NaNO_2$, $FeSO_4$, and H_2SO_4 in water, as described elsewhere.[13] It was purified by passage through 10 mol dm^{-3} KOH solution, a column of KOH pellets, and a trap cooled to −78 °C (CO_2–acetone). All reactions were carried out under nitrogen and all solvents were degassed with N_2 before use. All yields are quoted relative to the Zr-containing starting material.

I.r. spectra were recorded using a PE 297 spectrophotometer, and ^1H n.m.r. spectra were obtained using Varian HA100 or JEOL JMN-PMX 60 spectrometers. Elemental analyses were determined by the Microanalytical Laboratory of this Department.

Reaction between [Zr(η-C_5H_5)$_2Ph_2$] *and* NO: [Zr(η-C_5H_5)$_2$(Ph){ON(Ph)NO}].—A solution of phenyl-lithium (13 cm^3, 0.87 mol dm^{-3}) was added to a suspension of [Zr(η-C_5H_5)$_2Cl_2$] (1.5 g) in degassed diethyl ether (Na-dried, 20 cm^3) at −40 °C (chloroform–CO_2 slush-bath). The mixture was stirred at this temperature for 2 h, then warmed to 0 °C, and evaporated to dryness, the resulting solid being washed with n-pentane (50 cm^3) and dried *in vacuo*. The solid was extracted into benzene (50 cm^3) (**CAUTION:** carcinogen) and the solution filtered. The clear filtrate of [Zr(η-C_5H_5)$_2Ph_2$] was then treated with a stream of NO gas for 10—15 min. The resulting pale yellow solution was degassed with N_2 and evaporated to dryness, the remaining solid being twice recrystallised from benzene–n-hexane affording the complex as a white microcrystalline powder. The compound was dried *in vacuo* at 60—70 °C for 2—3 d (yield 0.98 g, 44%) (Found: C, 60.6; H, 4.9; N, 6.2. Calc. for $C_{22}H_{20}N_2O_2Zr$: C, 60.6; H, 4.6; N, 6.4%).

Preparation of [Zr(η-C_5H_5)$_2$Cl{ON(Ph)NO}].—Ag[ON(Ph)NO] (1.8 g) was added to a suspension of [Zr(η-C_5H_5)$_2Cl_2$] (2.0 g) in benzene (30 cm^3). The mixture was stirred in the dark for 2 d at room temperature, and the resulting solution filtered to remove AgCl, giving a pale yellow filtrate. This was reduced in volume *in vacuo* and treated with n-hexane. Further evaporation *in vacuo* afforded a white solid, and the mixture was then allowed to stand for 1 h to assist completion of crystallisation. The white complex was filtered off and dried *in vacuo* at 50 °C for 5 h (1.92 g, 71%) (Found: C, 48.5; H, 3.9; Cl, 9.2; N, 6.9. Calc. for $C_{16}H_{15}ClN_2O_2Zr$: C, 48.8; H, 3.8; Cl, 9.0; N, 7.1%).

[Zr(η-C_5H_5)$_2$Cl{ON(C_6H_4Me-*p*)NO}] was prepared similarly using [Zr(η-C_5H_5)$_2Cl_2$] (1.0 g) and Ag[ON(C_6H_4Me-*p*)NO] (1.0 g), and was isolated as a white solid (0.85 g, 61%) (Found: C, 49.7; H, 4.2; Cl, 8.6; N, 6.6. Calc. for $C_{17}H_{17}ClN_2O_2Zr$: C, 50.0; H, 4.2; Cl, 8.7; N, 6.9%).

Reaction of [Zr(η-C_5H_5)$_2Cl_2$] *with* [NH_4][ON(C_6H_4Me-*p*)NO].—[Zr(η-C_5H_5)Cl_2] (0.5 g) was added to a warm solution of [NH_4][ON(C_6H_4Me-*p*)NO] (0.58 g) in dry ethanol (50 cm^3). After a few seconds a white solid began to precipitate and the mixture was stirred at 50 °C for 2 h, and then cooled to room temperature. The white solid was filtered off, washed with light petroleum (b.p. 40—60 °C), and dried *in vacuo*. The compound was identified as [Zr{ON(C_6H_4Me-*p*)NO}$_4$] (0.48 g, 81%) (Found: C, 48.5; H, 4.1; N, 15.8. Calc. for $C_{28}H_{28}N_8O_8Zr$: C, 48.3; H, 4.1; N, 16.1%).

Using a 1:1 mol ratio of [Zr(η-C_5H_5)$_2Cl_2$] and [NH_4][ON(C_6H_4Me-*p*)NO], the same compound was obtained.

Alternative Preparation of [Zr{ON(C_6H_4Me-*p*)NO}$_4$].—To a suspension of $ZrCl_4$ (0.5 g) in dry benzene (50 cm^3) was added Ag[ON(C_6H_4Me-*p*)NO] (1.1 g). The mixture was stirred in the dark overnight and the white precipitate which had formed was filtered off and recrystallised from chloroform–light petroleum (b.p. 60—80 °C) mixtures. The *complex* was dried *in vacuo* (0.56 g, 76% based on the Ag^+ salt) (Found: C, 48.6; H, 4.1; N, 16.3. Calc. for $C_{28}H_{28}N_8O_8Zr$: C, 48.3; H, 4.1; N, 16.1%).

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