

THE NITROSONIUM ION, NO^+ , AND ITS VERSATILITY IN TRANSITION METAL ORGANOMETALLIC SYNTHESIS

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SUMMARY

The versatility of the nitrosonium ion, NO^+ , in organometallic synthesis is illustrated by its reactions with a variety of transition metal compounds. With the species $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3$, $\text{M}=\text{Co}$ and Rh , NOPF_6 reacts in methanol/toluene mixtures to give $[\pi\text{-C}_5\text{H}_5\text{M}(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]\text{PF}_6$. When $\text{M}=\text{Ir}$, however, protonation takes place to give the hydride $[\pi\text{-C}_5\text{H}_5\text{Ir}(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3\text{H}]\text{PF}_6$. Halogen-containing organometallics such as $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$, $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$ and $\text{Mn}(\text{CO})_5\text{Br}$ react with NOPF_6 in acetonitrile to give the complexes $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})]\text{PF}_6$, $[(\pi\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$ and $[\text{Mn}(\text{CO})_5(\text{CH}_3\text{CN})]\text{PF}_6$ in which the solvent has replaced the halide ligands. Finally NO^+ reacts as a one-electron oxidising agent towards $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}$ and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SCH}_3]_2$ giving $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}^+$ and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SCH}_3]_2^+$ respectively. Reasons for the formation of the different types of products are discussed.

INTRODUCTION

The nitrosonium ion has recently received attention as a reagent in the preparation of cationic nitrosyls of the type $\{\text{Fe}(\text{CO})_2(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+$, by replacement of carbon monoxide in the neutral $\text{Fe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ ¹, and as a one-electron oxidising agent towards species such as *trans*- $\text{Mn}(\text{CO})_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{Br}$ ². Our studies with this ion have shown that as well as behaving in the above manner it is considerably more versatile in its behaviour towards organometallics than has hitherto been realised. This paper seeks to point out the various reactions of NO^+ in acetonitrile, or in methanol/toluene mixtures, which can lead to cationic nitrosyls, hydrides and nitriles as well as products of one-electron oxidation.

RESULTS AND DISCUSSION

The nitrosonium ion was first used to prepare cationic nitrosyls by simple replacement of carbon monoxide from $\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_3$, to give $[\pi\text{-C}_5\text{H}_5\text{Re}(\text{CO})_2(\text{NO})]^+$ ³ and by addition to $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$ to give $\{\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{NO})\text{Cl}\}^+$ ⁴. We have found that in the series of compounds $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3$, $\text{M}=\text{Co}$, Rh and Ir , either carbonyl replacement to give nitrosyl complexes, or hydride

formation via protonation can occur depending on the central metal atom. Thus, in methanol/toluene mixtures NOPF_6 reacts with $\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3$ and $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3$ to give the cationic nitrosyls $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]^+\text{PF}_6^-$ and $[\pi\text{-C}_5\text{H}_5\text{Rh}(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]^+\text{PF}_6^-$ as purple and yellow crystalline solids respectively. These diamagnetic complexes are 1/1 electrolytes in acetone (Table 1) and, unlike the carbonyl species from which they are derived, are air-stable in the solid state and in polar solvents. The IR spectra of the new species exhibit one strong band in the region associated with coordinated nitric oxide, the high frequency values of between $1830\text{--}1850\text{ cm}^{-1}$ (Table 2) being typical of cationic nitrosyls. The proton NMR spectra of the complexes (Table 2) show peaks due to cyclopentadienyl and triphenylphosphine groups in the correct ratio of 1/3.

TABLE 1

ANALYTICAL, CONDUCTIVITY AND MELTING POINT DATA

Complex	Analysis found (calcd.) (%)			Conductivity ^c ($\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mole}^{-1}$)	M.p. (°C)
	C	H	N		
$[\pi\text{-C}_5\text{H}_5\text{Co}(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]^+\text{PF}_6^-$	49.1 (49.2)	3.7 (3.6)	2.4 (2.5)	147	Dec. > 150
$[\pi\text{-C}_5\text{H}_5\text{Rh}(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]^+\text{PF}_6^-$	46.0 (45.7)	3.5 (3.3)	2.3 (2.3)	132	194 (with dec.)
$[(\pi\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3\text{CN})_2][\text{PF}_6^-]_2$	30.7 (30.4)	3.0 (2.9)	4.9 ^a (5.1)	315 ^d	Dec. > 150
$[\text{Mn}(\text{CO})_5(\text{CH}_3\text{CN})]^+\text{PF}_6^-$	22.2 (22.1)	0.8 (0.8)	3.7 ^b (3.7)	143 ^d	Dec. > 135

^a Other analyses: Found: F, 41.4; P, 11.5; V, 8.5. Calcd.: F, 41.2; P, 11.2; V, 9.2%.

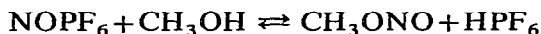
^b Other analyses: Found: Mn, 13.9; P, 7.7. Calcd.: Mn, 14.4; P, 8.1%.

^c 10^{-4} M in acetone at room temp.

^d Measured under nitrogen.

Although these species appear to react with sodium borohydride, methoxide ion and lithium halides we have been unable to isolate nitrosyl-containing products from the reaction mixtures.

The analogous reaction of NOPF_6 with $\pi\text{-C}_5\text{H}_5\text{Ir}(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3$ results only in the formation of the known hydride $[\pi\text{-C}_5\text{H}_5\text{Ir}(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3\text{H}]^+\text{PF}_6^-$.⁵ No evidence for a nitrosyl species has been found. The protonation reaction is possible since nitronium salts take part in the following equilibrium in methanol solution:



Such protonations have previously been encountered in the reactions of $\text{M}(\text{CO})_3\text{-}[\text{P}(\text{C}_6\text{H}_5)_3]_2$, $\text{M}=\text{Ru}$ and Os , to give $\{\text{M}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{H}\}^+$. The fact that protonation occurs with iridium, whereas nitrosyl formation takes place with Co and Rh is probably a reflection of the more basic nature of the complex of the third row element. The possibility that the use of a phosphine, L, less basic than $\text{P}(\text{C}_6\text{H}_5)_3$ in $\pi\text{-C}_5\text{H}_5\text{Ir}(\text{CO})\text{L}$ could promote formation of $[\pi\text{-C}_5\text{H}_5\text{Ir}(\text{NO})\text{L}]^+$ is under study. The alternative possibility, whereby a more basic phosphine L in $\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})\text{L}$ might lead to protonation on cobalt has been attempted using $\text{L}=\text{tricyclohexyl-}$

phosphine. In this case however, nitrosyl formation is still favoured to give $[\pi\text{-C}_5\text{H}_5\text{Co}(\text{NO})\text{P}(\text{C}_6\text{H}_{11})_3]\text{PF}_6$.

We have briefly reported on reactions of NOPF_6 in acetonitrile which give cationic acetonitrile complexes by cleavage of the metal-metal bond in $\text{M}_2(\text{CO})_{10}$, $\text{M}=\text{Mn}$ and Re , and by displacement of the arene group in (toluene) $\text{Cr}(\text{CO})_3$.⁶ Further investigations with this solvent show that organometallic compounds containing halogens coordinated to the metal react with NOPF_6 to give species in which the halide ligand is replaced by the solvent. In contrast to reactions described later, no oxidation takes place.

Thus, $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ reacts with NOPF_6 in acetonitrile to give the known $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{MeCN}]\text{PF}_6$.⁷ The physical properties of the compound are identical to those reported. However, this preparative route allows the complex to be isolated very rapidly in near quantitative yields, and represents a great improvement over the established synthesis⁸.

In a similar reaction, $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$ reacts with NOPF_6 to give the dication $[(\pi\text{-C}_5\text{H}_5)_2\text{V}(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$ as very dark green needles. The solid complex is fairly stable in air but its dark green-brown solutions in polar solvents are slowly decomposed. The IR spectrum exhibits two bands of medium intensity at 2325 cm^{-1} and 2350 cm^{-1} due to the coordinated nitrile ligands.

The expected paramagnetism of this formally V^{IV} complex is confirmed by both magnetic susceptibility and ESR measurements. Thus a magnetic moment of 1.69 B.M. has been found which is consistent with one unpaired electron. The room-temperature solution ESR spectrum consists of eight lines due to hyperfine splitting by the ^{51}V ($I=7/2$) nucleus. No ^{14}N ($I=1$) splitting was observed. The $\langle g \rangle$ value of 1.98, and the average hyperfine splitting due to ^{51}V of 75G are similar to the values found for the related V^{IV} complex $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$.⁹

$\text{Mn}(\text{CO})_5\text{Br}$ reacts with NOPF_6 in acetonitrile to give $[\text{Mn}(\text{CO})_5\text{CH}_3\text{CN}]\text{PF}_6$ as a white crystalline solid. It is obtained in lower yields than in the reaction of $\text{Mn}_2(\text{CO})_{10}$ and NOPF_6 .⁶ Other halo-organometallics such as $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ and $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ also react with the nitrosonium ion in acetonitrile but no products have been isolated.

The final mode of reaction of NOPF_6 we have noted is its behaviour as a one-electron oxidising agent. It has recently been shown that in weakly coordinating solvents such as CH_2Cl_2 or benzene, NO^+ oxidises species of the type *trans*- $\text{Mn}(\text{CO})_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{Br}$ to the corresponding $\{\textit{fac}\text{-Mn}(\text{CO})_3[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]_2\text{Br}\}^+$ cation.² In acetonitrile however, oxidation of Ni^{II} amines to the corresponding Ni^{III} species was found to occur with coordination of an acetonitrile ligand¹⁰. We have found that even in acetonitrile, one-electron oxidations can be carried out without incorporation of solvent in the products. Thus ferrocene and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SCH}_3]_2$ are oxidised to the ferricinium and $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SCH}_3]_2^+$ cations respectively. It is pertinent to note here that carbonyl containing species such as $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{SR}]_2$ can theoretically undergo either oxidation or nitrosyl replacement reactions. The main factor governing the type of product formed is the oxidation potential of the organometallic complex. It has been shown in the field of transition metal dithiolene chemistry that considerable variation in oxidation and reduction potentials can be caused by the variation of substituent, R, in such species as $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_z$ ($z=2$ or 3)¹¹. Thus, if by changing $\text{R}=\text{CH}_3$ to a more electron-with-

TABLE 2
 INFRA-RED AND PROTON MAGNETIC RESONANCE SPECTRAL DATA

Complex	IR stretching frequencies (cm^{-1})			NMR resonances ^a			
	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{N}=\text{O})$	$\nu(\text{C}\equiv\text{N})$	Medium	C_6H_5^b	$\text{C}_6\text{H}_{11}^b$	C_3H_5
$[\pi\text{-C}_3\text{H}_5\text{Co}(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]\text{PF}_6$		1847 s		Nujol			
		1848 s		CH_2Cl_2	2.22 (mult.)		4.22 s
$[\pi\text{-C}_3\text{H}_5\text{Co}(\text{NO})\text{P}(\text{C}_6\text{H}_{11})_3]\text{PF}_6$		1848 s		Nujol			
		1840 s		CH_2Cl_2		8.15 (brd. mult.)	4.06 s
$[\pi\text{-C}_3\text{H}_5\text{Rh}(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]\text{PF}_6$		1838 s		Nujol			
		1831 s		CH_2Cl_2	2.25 (mult.)		4.02 s
$[(\pi\text{-C}_3\text{H}_5)_2\text{V}(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$			2325 m	KBr			
			2350 (sh)	disc			
$[\text{Mn}(\text{CO})_5(\text{CH}_3\text{CN})]\text{PF}_6$	2140 w			$(\text{CH}_3)_2\text{CO}$			
	2061 vs						
	2043 (sh)						

^a τ scale measured in deuterioacetone at 40° (TMS reference).

^b Values refer to centre of asymmetric peaks.

drawing group such as $R = CF_3$ in $[\pi-C_5H_5Fe(CO)SR]_2$ the oxidation potential can be raised sufficiently to disallow oxidation by NO^+ , nitrosyl formation might be preferred. This possibility is being investigated.

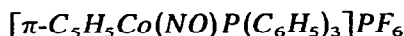
CONCLUSION

The results reported here show that the mode of reaction of NO^+ is highly dependent on the solvent system used, and on such properties as the Lewis basicity or redox potential of the reacting organometallic. By consideration of these possible factors, the nitrosonium ion can be used in the preparation of a very wide range of cationic organometallic compounds.

EXPERIMENTAL

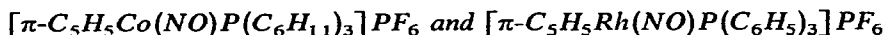
All reactions involving nitrosonium salts were carried out under an atmosphere of nitrogen and in dried, degassed solvents. $Mn(CO)_5Br^{12}$, $\pi-C_5H_5M(CO)L$, $M = Co$, $L = P(C_6H_5)_3$, $P(C_6H_{11})_3$, $M = Rh$, $L = P(C_6H_5)_3^{13}$, and $\pi-C_5H_5Fe(CO)_2I^{14}$ were prepared by published methods, $NOPF_6$ was purchased from Ozark-Mahoning Company and $(\pi-C_5H_5)_2VCl_2$ from Alfa Inorganics Ltd.

Micro-analyses were carried out by the microanalytical service of this department and Galbraith Inc. Knoxville, Tennessee. IR spectra were recorded on Perkin-Elmer PE 257 and Beckman IR8 spectrophotometers; NMR spectra were recorded on the Varian T60 instrument.

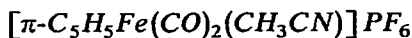


To 0.42 g of $\pi-C_5H_5Co(CO)P(C_6H_5)_3$ in a mixture of 20 ml benzene (or toluene) and 10 ml methanol was added 0.27 g of solid $NOPF_6$. The red solution became dark purple-brown and carbon monoxide was evolved.

After stirring had been continued for 10 min the product began to separate as a dark purple solid. Addition of ether (approximately 25 ml) completed the precipitation. The complex was recrystallised from dichloromethane/hexane to give 0.46 g of $[\pi-C_5H_5Co(NO)P(C_6H_5)_3]PF_6$ as dark purple crystals. Yield: 81% based on $\pi-C_5H_5Co(CO)P(C_6H_5)_3$. $[\pi-C_5H_5Co(NO)P(C_6H_5)_3]PF_6$ is soluble in polar solvents such as dichloromethane and acetone to give air-stable purple-brown solutions.



These were prepared by the above method in 38% and 84% yields respectively. They are air-stable purple-brown and yellow complexes respectively with properties similar to those of $[\pi-C_5H_5Co(NO)P(C_6H_5)_3]PF_6$.



To 0.6 g of $\pi-C_5H_5Fe(CO)_2I$ in 10 ml of acetonitrile was added 0.35 g of solid $NOPF_6$. The initial brown solution rapidly became deep orange and NO gas was evolved. After stirring for 5 min the solution was filtered and 100 ml of ether added. The resulting yellow crystalline solid (0.65 g) was dissolved in acetone and rapidly

precipitated by adding ether. The yellow product was filtered, washed well with ether and air-dried to give 0.57 g of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})]\text{PF}_6$. Yield: 79% based on $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$.



To a green solution of 0.5 g $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$ in 15 ml acetonitrile was added an excess of solid NOPF_6 (about 0.5 g). The resulting dark green-brown solution was stirred for 10 min, filtered and then treated with 50 ml ether. After 15 min the oil which had separated was isolated by decantation from the mother liquor. Slow evaporation at the water pump of an acetone solution of the oil gave, in the presence of methanol, very dark green needles of the product. Yield: 0.33 g, 30% based on $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$. $[(\text{C}_5\text{H}_5)_2\text{V}(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$ gives deep green-brown solutions in polar solvents such as acetonitrile and acetone. The compound is slowly decomposed in the solid state and more rapidly decomposed in solution.



To a pale yellow solution of 0.3 g of $\text{Mn}(\text{CO})_5\text{Br}$ in 10 ml of acetonitrile was added an excess of solid NOPF_6 (about 0.35 g). NO gas was evolved as the solution was rapidly stirred. After 5 min the dark yellow solution was filtered. On addition of approximately 50 ml of ether an off-white solid formed which, when dissolved in acetone and precipitated by ether, gave 0.09 g of white micro-crystals of the product. Yield: 22% based on $\text{Mn}(\text{CO})_5\text{Br}$. $[\text{Mn}(\text{CO})_5(\text{CH}_3\text{CN})]\text{PF}_6$ is soluble in acetone and acetonitrile to give colourless solutions which slowly decompose in air.

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