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Trityl Thionitrite: a Potential Transfer Nitrosating Agent for Metal Nitrosylation

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Abstract

Several known nitrosyl complexes of Ru, Rh, Ir, Co, Mo and W have been synthesized using trityl thionitrite as nitrosylating agent at elevated temperatures. Reactions of trityl thionitrite with different salts of Cr, Fe, Co and complexes of Ni, Pd and Pt whose nitrosyls have been obtained only at lower temperatures failed to yield their nitrosyls.

Introduction

In a study relating to the possible transition metal nitrosyl synthesis, trans-nitrosation has been widely used [1]. A range of transfer nitrosating agents like alkylnitrites nitrosamines, NOX ($X = Cl^-$, Br^-, Br_3^-, NO_2^-) have been used for the purpose. In these systems, advantage has been taken of the weakness of the O–N and N–N bonds. Literature survey, however, indicates practically no work towards *in situ* trapping of NO generated by weak S–NO bond cleavage, despite their many applications to effect nitrosation of amines and alcohols [2]. The S-nitroso compounds may be suited for such a study because of very large variations in their half lives and decomposition temperatures. Thus thionitrites, decomposing at elevated temperatures may possibly be able to nitrosylate metals which yield their nitrosyls only at higher temperatures and vice versa. This note concentrates on examining the applicability of trityl thionitrite (hereafter referred as TTN) [3] as a potential nitrosylating agent by synthesizing literature known metal nitrosyls.

Experimental

The chemicals used were of Analar grade. TTN and the starting complexes of all the metal ions were prepared and purified by literature procedures [4–23]. Carbon, hydrogen, nitrogen and halide analyses followed ref. 24. IR spectra (4000–200 cm^{-1}), melting points (m.p.) and magnetic susceptibilities of the complexes were recorded as described elsewhere [25]. Some of the results are given in Table 1.

In a typical reaction 10 ml of solution containing 0.5 mmol of the appropriate metal salt or complex in a suitable solvent and 1.0 mmol of TTN dissolved in CH_2Cl_2 (10 ml) were successively added with vigorous stirring to a boiling solution of coligand (2.0 mmol) dissolved in the same solvent under nitrogen. The resulting reaction mixture was heated under reflux for some time (Table 1) either in the presence of $HgCl_2$ or dry HCl gas (dry Cl_2 gas in the case of $Mo(CO)_6$). On cooling the refluxed solution to room temperature, metal nitrosyls were separated in most of the cases. The product was collected by filtration washed successively with ethanol, water, ethanol, ether and dried *in vacuo*. In cases where nitrosyls did not precipitate, like in the reactions with $W(CO)_6$ and $Mo(CO)_6$, the refluxed solution was concentrated under reduced pressure to half its volume. Addition of excess hexane to the concentrate precipitated the crystalline compound which was filtered, washed with hexane and dried *in vacuo*.

In the reaction of $[RuH(CO)Cl(PPh_3)_3]$ with TTN in the presence of $HgCl_2$ or dry HCl gas, shiny yellow crystals were obtained; the analytical data and the IR spectrum indicated them to be a mixture of two compounds. Since one of the components was relatively more soluble in benzene the components were separated by fractional crystallization using CH_2Cl_2 and benzene. The benzene fraction was crystallized using light petroleum ether, the second using CH_2Cl_2/MeOH. The benzene soluble fraction (m.p. 228 °C) analysed as $[Ru(NO)Cl_3(PPh_3)_2]$. The product which crystallized from CH_2Cl_2/MeOH, was identified as $[Ru(CO)_2Cl_2(PPh_3)_2]$ (m.p. 233 °C).

The nytrosylation reactions with the metal ions whose nitrosyls could be synthesized only at low temperatures (Cr, Fe, Co, Ni, Pd and Pt) were not successful.

Results and Discussion

The known thermal instability [26] of TTN allowed the nitrosylation reactions of the metal ions

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TABLE 1. Reactions, Conditions, Products Obtained, Colour, Melting Point and Position of NO of the Complexes

Sample no.	Reactants used (reaction condition) (specific reaction condition)	Solvent	Reaction products (colour, melting point (°C))	NO ($\mathrm{cm^{-1}}$)
1	$\mathrm{RuCl_3 \cdot {\it x}H_2O}$ + $\mathrm{EPh_3}$ + TTN (0.5 mmol) (2.0 mmol) (1.0 mmol) [(A), (C)] (E = P, As, Sb)	Et	$[\mathrm{Ru(NO)Cl_3(EPh_3)_2}]$	
2	$[\mathrm{RuCl_2(PPh_3)_3}]$ + TTN, $[\mathrm{RuCl_2(PPh_3)_4}]$ + TTN, $[\mathrm{RuH_2(PPh_3)_3}]$ + TTN, $[\mathrm{RuCl_3 \cdot (PPh_3)_2 \cdot MeOH}]$ + TTN, $[\mathrm{Ru(cp)Cl(PPh_3)_2}]$ + TTN or $[\mathrm{Ru(CO)Cl_2(PPh_3)_3}]$ + TTN [(B) (C)]	Et/DM (1:1) mixture	$[\mathrm{Ru(NO)Cl_3(PPh_3)_2}]$ (orange, 228)	1875
3	$[\mathrm{RuCl_2(PPh_3)_3}]$ + TTN, $[\mathrm{RuCl_2(PPh_3)_4}]$ + TTN, $[\mathrm{RuH_2(PPh_3)_3}]$ + TTN, $[\mathrm{RuCl_3(PPh_3)_2 \cdot MeOH}]$ + TTN, $[\mathrm{Ru(cp)Cl(PPh_3)_2}]$ + TTN or $[\mathrm{Ru(CO)Cl_2(PPh_3)_3}]$ + TTN [(B), (D)]	Et/DM (1:1) mixture	$[\mathrm{Ru_2(NO)Cl_4S_{1/2}(PPh_3)_2}]$ (brown–black, 280)	1875
4	$\mathrm{RuCl_3 \cdot {\it x}H_2O}$ + $\mathrm{EPh_3}$ + TTN [A, C]	Et	$[\mathrm{Ru_2(NO)Cl_4S_{1/2}(PPh_3)_2}]$ (brown–black, 280)	1875
5	$[\mathrm{RuCl_3(AsPh_3)_3}]$ + TTN, $[\mathrm{RuCl_3(AsPh_3)_2]MeOH}$ + TTN, $[\mathrm{Ru(cp)Cl(AsPh_3)_2}]$ + TTN, or $[\mathrm{Ru(CO)Cl_2(AsPh_3)_3}]$ + TTN [B, C]	Et + DM (1:1) mixture	$[\mathrm{Ru(NO)Cl_3(AsPh_3)_2}]$ (orange, did not melt)	1860
6	$[\mathrm{RuCl_3(AsPh_3)_3}]$ + TTN, $[\mathrm{RuCl_3(AsPh_3)_2 \cdot MeOH}]$ + TTN, $[\mathrm{Ru(cp)Cl(AsPh_3)_2}]$ + TTN, or $[\mathrm{Ru(CO)Cl_2(AsPh_3)_2}]$ + TTN [B, D]	Et + DM (1:1) mixture	$[\mathrm{Ru_2(NO)_2Cl_4S(AsPh_3)_2}]$	1800 (broad)
7	$[\mathrm{RuH(CO)Cl(PPh_3)_3}]$ + TTN	Et	$[\mathrm{Ru(NO)Cl_3(PPh_3)_2}]$ (orange, 228 °C)	1875
			+	
			$[\mathrm{Ru(CO)_2Cl_2(PPh_3)_2}]$ (yellow, 233 °C)	1990, 2065 (ν_{CO})
8	$[\mathrm{RuCl_2\{(OPh_3)_3P\}_4}]$ + TTN	Et + DM	$[\mathrm{Ru(NO)Cl_3\{(OPh_3)_3P\}_2}]$ (yellow, 242 °C)	1900
9	$\mathrm{RhCl_3 \cdot {\it x}H_2O}$ + $\mathrm{EPh_3}$ + TTN (0.5 mmol) (2.0 mmol) (1.0 mmol) [A, C] (E = P, As)	Et	$[\mathrm{Rh(NO)Cl_2(EPh_3)_2}]$	
10	$\mathrm{RhCl_3 \cdot {\it x}H_2O}$ + $\mathrm{PPh_3}$ + TTN + $\mathrm{NaBH_4}$ [A, C]	Et	$[\mathrm{Rh(NO)(PPh_3)_3}]$ (orange)	1635
11	$[\mathrm{RhCl(EPh_3)_3}]$ + TTN (E + P, As)	Et + DM	$[\mathrm{Rh(NO)Cl_2(EPh_3)_2}]$	
12	$[\mathrm{Rh(CO)Cl(EPh_3)_3}]$ + TTN [B, C] (E = P, As)	Et + DM	$[\mathrm{Rh(NO)Cl_2(EPh_3)_2}]$	
13	$[\mathrm{RhCl(PPh_3)_2]_2}$ + TTN or $[\mathrm{RhH(PPh_3)_4}]$ + TTN [B, C]	Et + DM Et + DM	$[\mathrm{Rh(NO)Cl_2(PPh_3)_2}]$ (orange, 224 °C)	1640

(continued)

TABLE 1. *(continued)*

Sample no.	Reactants used (reaction condition) (specific reaction condition)	Solvent	Reaction products (colour, melting point (°C))	NO (cm^{-1})
14	$[RhH(CO)(PPh_3)_3]$ + TTN (B, C]	Et + DM	$[Rh(CO)(NO)Cl_2(PPh_3)_2]$	1635, 1965 (ν_{CO})
15	$[RhH\{(OPh_3)_3P\}_4]$ + TTN	Et + DM	$[Rh(NO)Cl_2\{(OPh_3)_3P\}_2]$	1635
16	$IrCl_3 \cdot xH_2O$ + PPh_3 + TTN (0.5 mmol) (2.0 mmol) (1.0 mmol)	2-MEt	$[Ir(NO)Cl_2(PPh_3)_2]$	1565
17	$CoCl_2 \cdot 6H_2O$ + en + TTN (3.0 mmol) (12.0 mmol) (6.0 mmol)	Mt	$[Co(en)_2Cl(NO)]Cl$	1640
18	$[M(CO)_6]$ + PPh_3 + TTN (1 mmol) (6.0 mmol) (3.0 mmol) (M = Mo, W) [B, E]	BN	$[\{MCl_2(PPh_3)_2\}_2N_2O_2]Cl_2$ (yellow–green, 165–170 °C)	1135, 1045, 990

Et = C_2H_5OH; DM = CH_2Cl_2; Mt = CH_3OH, 2-MEt = 2-methoxy ethanol; BN = benzene. A = The reaction mixture was refluxed for 30 min under vigorous stirring. B = The reaction mixture was refluxed for about 2 h under vigorous stirring. C = The reaction was carried out in the presence of $HgCl_2$ or dry HCl gas. D = The reaction was carried out in the absence of $HgCl_2$ or HCl gas. E = A slow stream of dry chlorine gas was passed through the reaction mixture.

and their complexes. It is obvious from the results of the reactions, that the method has synthetic potential only for those metal nitrosyls which are formed and stable at relatively higher temperatures. Since the prepared nitrosyls were known ones, they have been characterized by chemical analyses, and by comparing their colours, m.p., mixed m.p., spectra (IR, UV, Vis) and magnetic data with those of metal nitrosyls prepared by other literature methods.

Table 1 also indicates a few reactions which gave unexpected nitrosyl complexes. These are discussed below.

(i) Reaction of $[RuH(CO)Cl(PPh_3)_2]$ with TTN in the presence of either $HgCl_2$ or dry HCl gas yielded a yellow shiny microcrystalline compound, different from the known nitrosyl $[Ru(NO)(CO)Cl(PPh_3)_2]$ [20] prepared by using MNTS (*N*-nitrosomethyl-*p*-toluenesulphonamide). Spectral and analytical data of the product indicated it to be a mixture of two compounds. Its IR spectrum exhibited three intense bands at 1995, 2065 (ν_{CO}) and 1875 (ν_{NO}) cm^{-1}. These after separation by fractional crystallization using benzene/dichloromethane were found to be well known nitrosyls, $[Ru(NO)Cl_3(PPh_3)_2]$ and $[Ru(CO)_2Cl_2(PPh_3)_2]$.

(ii) Reactions of $Mo(CO)_6$ and $W(CO)_6$ with TTN in the presence of PPh_3 or $AsPh_3$ and dry chlorine gas yielded compounds having empirical formulae $[\{MCl_2(EPh_3)_2\}_2N_2O_2]Cl_2$ (M = Mo, W, E = P, As). *Anal.* Calc. for $[\{MoCl_2(PPh_3)_2\}_2N_2O_2]Cl_2$: C, 56.9; H, 3.9; N, 1.8; Cl, 14.1. Found: C, 56.6; H, 4.2; N, 2.1; Cl, 13.7%. Calc. for $[\{WCl_2(PPh_3)_2\}_2N_2O_2]Cl_2$: C, 51.0; H, 3.54; N, 1.7; Cl, 12.6. Found: C, 50.4; H, 3.9; N, 2.2; Cl, 13.2%. Their IR spectra displayed bands around 1145, 1034 and 980 cm^{-1}, characteristic for a bridging $N_2O_2^{2-}$ group, coordinated through oxygen atoms [27]. A similar reaction of $Mo(CO)_6$ with MNTS yielded a dinitrosyl complex [28, 29]. Formation of the $N_2O_2^{2-}$ complex in place of a dinitrosyl, implied the possibility of a different reaction path. It is well established that in the presence of a Lewis base, denitrosation of thionitrites proceeds with the formation of $H_2N_2O_2$ [30]. Presuming EPh_3 acts as a base as well as being a coligand, the generated $H_2N_2O_2$ interacts with $M(CO)_6$ yielding their $N_2O_2^{2-}$ complexes in the presence of chlorine gas. The latter may be serving as an oxidant to take Mo from zero to the +5 state and a source of chlorine ion as well.

The reactions carried out with other metal ions in the presence of PPh_3, should also have yielded $N_2O_2^{2-}$ complexes if the EPh_3 molecules are acting as a base. In such cases the relative stability of $N_2O_2^{2-}$ complexes compared to that of nitrosyl ought to be playing an important role in deciding the course of the reaction.

(iii) Reaction of $RuCl_3 \cdot xH_2O$ with TTN in the presence of PPh_3 or $AsPh_3$ in ethanol in the absence of $HgCl_2$ or dry HCl gas yielded a reddish brown microcrystalline complex with an empirical formula $[Ru(NO)Cl_2S_{1/2}EPh_3]$. These complexes did not melt upto 300 °C. When this complex was heated to reflux with excess PPh_3 or AsPh in dichloromethane or chloroform it yielded pure $[Ru(NO)Cl_3(EPh_3)(E'Ph_3)]$ (E = E' = P or As). Ruthenium complexes having EPh_3 as coligands, on reacting with TTN in the absence of $HgCl_2$ or HCl gas also yielded the same brown compound.

Reaction of $RhCl_3 \cdot xH_2O$ with TTN in the presence of PPh_3, $AsPh_3$ or $SbPh_3$ yielded pure nitrosyl complexes $[Rh(NO)Cl_2L_2]$ ($L = PPh_3, AsPh_3$ or $SbPh_3$). The same compounds were also obtained in the presence of HCl gas or $HgCl_2$.

In most of the reactions described herein, Rh and Ir were introduced in the +1 oxidation state while the isolated complexes have the metals in the +3 oxidation state. NO in these complexes is behaving as one electron donor. It appears that during the formation of the complexes the metal ions are oxidized by the NO radical or by NO^+ formed by the homo or heterolytic cleavage of the S–N bond of thionitrites.

Although it seems probable that metal nitrosylation could arise by prior formation of HNO_2 or NOX which subsequently nitrosylate the metal ions, at present it is not possible to decide whether the reaction is a one pot reaction or a multistep one. It seems, however, fairly certain that thionitrites can effect the nitrosylation of metal ions and compare well with other nitrosylating agents.

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