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REACTIONS OF $Ru_3(CO)_{12}$ WITH NITROBENZENE AND ANILINE

E. SAPPA and L. MILONE

Institute of Chemistry of the University, Turin (Italy)

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SUMMARY

Nitrobenzene and aniline react with $Ru_3(CO)_{12}$ to yield the following trinuclear compounds: $Ru_3(CO)_{10}NPh$, $Ru_3(CO)_9(NPh)_2$, $HRu_3(CO)_{10}NHPh$, and $H_2Ru_3(CO)_9NPh$. Structural proposals for those products are made on the basis of instrumental analysis. Their properties are described and some comments on their reactivity are made.

INTRODUCTION

The successful reduction of nitrobenzene to aniline was reported by Calderazzo *et al.*[1] who used hydrogen at high pressures in presence of $Ru_3(CO)_{12}$ or other ruthenium compounds; the formation of nitrenes stabilized by complexation on the metal, and of hydridocarbonyls in the hydrogen transfer step was postulated.

A number of organonitrogen iron carbonyl derivatives, is known, some of which contain nitrene ligands[2]. In particular Dekker and Knox[2], by treating $Fe_2(CO)_9$ with CH_3NO_2 or CH_3N_3, and Stanghellini-Rossetti[3] by treating $Fe_3(CO)_{12}$ with $C_6H_5NO_2$ obtained respectively the trinuclear compounds $Fe_3(CO)_9(NCH_3)_2$ and $Fe_3(CO)_9(NC_6H_5)_2$; the structure of the former product, determined by Doedens[4] was shown to have close analogy with the chalcogen compounds $Fe_3(CO)_9E$ (E=S, Se, Te)[5]. Moreover Koerner von Gustorf and Wagner[6] obtained $Fe_3(CO)_{10}NSi(CH_3)_3$ which exhibits a face-bonded CO group[7]. In all these compounds, a NR group acts as a triply bonded, four electron donor.

Finally, Baikie, Mills *et al.* obtained the compounds $Fe_2(CO)_6(HN \cdot NCR_2)_2$[8] and $Fe_3(CO)_9(N \cdot NCR_2)_2$[9], where R=H, Ar; and observed that nitrogen is capable of coordination to a polynuclear metal system "in ways at least as varied as carbon..."[9].

As a part of our studies on the reactivity of $Ru_3(CO)_{12}$ we have treated $Ru_3(CO)_{12}$ with nitrobenzene and aniline under mild conditions, in order to isolate organonitrogen–ruthenium compounds which might conceivably act as intermediates in the reduction of nitrobenzene. Aniline was treated also, because Deeming and Underhill[10] recently emphasized the ability of some trinuclear carbonyls to extract hydrogen from H_2X molecules, where X is a carbon- or sulphur-containing ligand, which can act as a four electron donor and triply bridge the three metal atoms.

We obtained the products $Ru_3(CO)_{10}NPh$ (I), $Ru_3(CO)_9(NPh)_2$ (II), $HRu_3(CO)_{10}HNPh$ (III) and $H_2Ru_3(CO)_9NPh$ (IV) from the above reactions. In this paper we describe some of the properties of these compounds, together with comments on their reactivity. We also propose structures for the compounds.

EXPERIMENTAL

Conventional glass vessels, equipped with reflux condenser and magnetic stirrer were used. Benzene, previously distilled and dried, was used as solvent, under a dry nitrogen atmosphere. $Ru_3(CO)_{12}$ was purchased from Strem Chemicals: nitrobenzene and aniline were purified according to literature methods, phenylisocyanate and phenylisothiocyanate (Fluka) were used without further purification.

The reactions were followed by means of IR spectra and TLC.

When hydrogen (high-purity commercial gas, dried before use) was employed, stainless-steel pressure reactors were used, stirred and warmed in an oil bath.

Table 1 lists the reaction conditions, and the yields of TLC-purified products (Kieselgel P.F.: eluent petroleum ether) obtained. Elemental analyses were obtained using a C, H, N analyzer, and a Perkin–Elmer 303 Model Atomic Absorption Spectrophotometer: IR spectra were recorded on a Beckman IR-12 (KBr optics); the NMR spectra were obtained on a JEOL JNM C-60 HL instrument and mass spectra on an Hitachi–Perkin–Elmer RMU-6H spectrometer. The elemental analyses of the products were as follows: Found: C, 28.73; H, 1.05; N, 2.15; Ru, 44.7. $C_{16}H_5NO_{10}Ru_3$ calcd.: C, 28.41; H, 0.74; N, 2.07; Ru, 45.1%. Found: C, 33.97; H, 1.76; N, 3.88; Ru, 41.8. $C_{21}H_{10}N_2O_9Ru_3$ calcd.: C, 34.11; H, 1.36; N, 3.79; Ru, 41.3%. Found: C 29·1; H, 1.21; N, 2.33; Ru, 44.76. $C_{16}H_7NO_{10}Ru_3$ calcd.: C, 28.33; H, 1.04; N, 2.06; Ru, 45.0%. Found: C, 28.13; H, 1.34; N, 2.03; Ru, 47.8. $C_{15}H_7NO_9Ru_3$ calcd.: C, 27.70; H, 1.08; N, 2.15; Ru, 46.9%.

The physical characteristics, and IR and NMR spectra of the products, are listed in Table 2.

TABLE 1

REACTIONS BETWEEN $Ru_3(CO)_{12}$ AND NITROGEN COMPOUNDS, IN BOILING BENZENE

Reactant	*Molar ratio of reactant/$Ru_3(CO)_{12}$*	*Reaction time (min)*	*Product yields (%)*[a]
$PhNO_2$	20/1	45	(A) 70, (I) 10
$PhNO_2$	20/1	120	(A) 40, (I) 15, (II) 10.
$PhNO_2$	20/1	195	(A) 30, (I) 10, (II) 15.
PhNCO	10/1	195	(A) 40, (I) 20.
PhNCO	20/1	480	(A) 40, (I) 20, (II) tr.
PhNCS	10/1	390	Two unidentified products.
$PhNH_2$	30/1	60	(A) 20, (III) 20, (B) tr.
$PhNH_2$	20/1	120	(A) 10, (III) 35, (B) tr.
$PhNH_2$	20/1	180[b]	(A) tr., (III) 30, (B) tr.

[a] (A) $=Ru_3(CO)_{12}$, (B) $=H_4Ru_4(CO)_{12}$, tr.=traces. Yields calculated on the carbonyl.

[b] Reaction times longer than 180 min resulted in very low yields of (III); aniline condensation products were observed.

TABLE 2

PHYSICAL PROPERTIES IR AND NMR SPECTRA OF THE TRINUCLEAR ORGANONITROGEN RUTHENIUM COMPOUNDS

Compound	*Physical properties*	*Mol. weight*[a]	*IR spectra* (CCl_4)[b]	*NMR* (CCl_4) (τ)
$Ru_3(CO)_{10}NPh$	Lemon-yellow crystals m.p. 120° (dec.)	677	2104 m, 2070 vs, 2032 vs, 2011 s(sh), 1978 w, 1743 s. 1260 m, 1229 s, 1217 m(sh)	3.05 s
$Ru_3(CO)_9(NPh)_2$	Orange crystals m.p. 125–130° (dec.)	740	2073 vs, 2049 vs, 2021 s(sh) 2014 vs, 1990 m, 1980 w(sh) 1260 s, 1235 m(sh), 1218 s.	3.10 m
$HRu_3(CO)_{10}NHPh$	Red crystals m.p. gradual dec.	679	3376 w 2101 m, 2065 vs, 2051 vs, 2026 vs, 2011 vs, 2003 vs(sh) 1982 m. 1214 s.	3.08 m (5 H) 3.85 br (1 H) 23.3 d (1 H)
$H_2Ru_3(CO)_9NPh$	Yellow crystals m.p. 130–140° (dec.)	651	2115 s, 2080 vs, 2057 vs, 2049 s(sh), 2013 vs, 2000 s(sh) 1989 s(sh)	2.85 s (5 H) 27.8 s (2 H)

[a] Found by mass spectrometry. [b] The C–N stretching frequency was recorded using CS_2 solutions.

RESULTS

Reactivity of the products. Compounds (I), (II) and (III) were formed respectively from nitrobenzene and aniline. $Ru_3(CO)_{12}$ was also treated with PhNCO and PhNCS, but whereas PhNCO gave (I) in good yields and (II) in only trace amounts, PhNCS yielded only unidentified rubber-like carbonyls. It seems likely that polymeric substances are obtained because of the presence of sulphur. Similar behaviour has already been observed in the reactions between $Ru_3(CO)_{12}$, thiols and organic disulphides[11,12].

Compound (I) reacts in boiling benzene (90 min) with excess of $PhNO_2$ to give (II) in 30% yield together with products of decomposition. Reaction of (I) under hydrogen pressure (20 atm, 85°, 120 min) in benzene was also attempted, and yielded (IV) (80%) together with $H_4Ru_4(CO)_{12}$.

Mass spectra. The mass spectra were all recorded in presence of internal standards (perfluoroalkanes). All products show the parent ion.

In particular (I) exhibits gradual loss of ten CO units, followed by HCN and C_2H_2, and complete fragmentation of the organic moiety; Ru_3^+ is observed in very low abundance, whereas the ions $Ru_3(CO)_nNPh^{2+}$ ($n=8$–0), in particular Ru_3NPh^{2+}, are very abundant.

(II) loses 9 CO units, followed by the release of two HCN units and fragmentation of the phenyl groups, with loss of C_2H_2, C_2 and C; the ions $Ru_3(CO)_9(NPh)_2^{2+}$ ($n=4$–0) are observed but Ru_3^+ is not detected. Neither bi- nor mononuclear fragments were observed, in contrast with the behaviour of $Fe_3(CO)_9(NPh)_2$[3] which yields nitrogen-containing binuclear fragments.

(III) loses 3 CO units, followed by the concurrent loss of CO and of H, and finally the further CO units are released; fragmentation of the organic moiety is also observed with loss of $HNCH_2$ and C_2H_2; Ru_3^+ is not observed, and of the doubly charged fragments, only Ru_3NPh^{2+} is abundant. Peaks at 93 and 92 *m/e* were also observed, corresponding to $PhNH_2^+$ and $PhNH^+$.

(IV) loses one CO, then CO and H_2 concurrently and finally the remaining CO groups; fragmentation of the organic moiety also occurs with loss of HCN, C_2H_4, C_2. Ru_3^+ is detected in very low abundance, whereas the $Ru_3(CO)_nNPh^{2+}$ (n=6–0) are relatively intense. Some binuclear fragments, in particular Ru_2NPh^+ were also detected. The abundance of the trinuclear fragments is 90.6%, which is comparable with those of $H_2Ru_3(CO)_9C_2Ph_2$ and $H_2Ru_3(CO)_9E$ (E=S, Se, Te).

NMR spectra. In CCl_4 solutions (I) and (II) show phenyl absorptions only; (III) displays a very interesting absorption pattern with one phenyl, one NH and one hydridic hydrogen couplet with the NH, as shown by spin decoupling techniques ($J \simeq 1.5$ Hz).

(IV) shows a phenyl group and a sharp singlet due to two bridged hydridic atoms, in the same region as observed for $H_2Ru_3(CO)_9E$ and $H_2Ru(CO)_9R$ (R= C_2Ph_2, C_8H_{12}, C_8H_8)[13–15]; this indicates that, at room temperature, the two hydrides are equivalent.

IR spectra. With the exception of (I), all the compounds show only two terminal CO absorptions; also they all have C–N bonds. In particular, (I) shows a strong absorption at 1743 cm^{-1} which is in accordance with a face-bonded CO, and which is broadened and shifted to 1723 cm^{-1} in $CHCl_3$. The spectrum of (II) is similar to the spectra of the $Fe_3(CO)_9(NR)_2$ complexes; the spectrum of (IV) is analogous to those of $H_2Ru_3(CO)_9E$ (E=S, Se, Te). Compound (III) has a weak absorption at 3376 cm^{-1} which is assigned to the NH group.

DISCUSSION

From the results, there is evidence that $Ru_3(CO)_{12}$ in reacting with nitrogen-containing compounds, can given an even greater variety of stable trinuclear compounds than can $Fe_3(CO)_{12}$; and that, depending upon the nature of the organic compounds and on the reaction conditions, $Ru_3(CO)_{12}$ can form non-hydridic as well as hydridic compounds in particular, the latter when hydrogen abstraction from the organic molecule is possible, or when hydrogen is present. The absence of binuclear nitrogen-substituted ruthenium compounds from these reactions, as well as the very high abundance of the trimetallic fragments in the mass spectra, are indicative of the greater stability of the $Ru_3(CO)_{12}$ cluster with respect to $Fe_3(CO)_{12}$.

$Ru_3(CO)_{10}NPh$ is presumably the first product of the reaction between $Ru_3(CO)_{12}$ and the proposed nitrene species; one of its CO groups is easily substituted by NPh and H_2 without destruction of the cluster to give (II) and (IV) respectively. This indicates that one CO is differently bonded, and supports the IR findings; for (I) we therefore propose a structure analogous to the known $Fe_3(CO)_{10}NSi(CH_3)_3$[7]. The structure of (II) is presumably similar to those reported for the homologous iron compounds[2,3].

$H_2Ru_3(CO)_9NPh$ is not obtained directly from $Ru_3(CO)_{12}$ either in water–methanol basic solution, or in benzene*; it is formed only from (I) under a hydrogen

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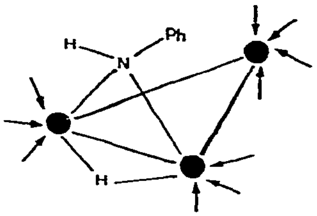
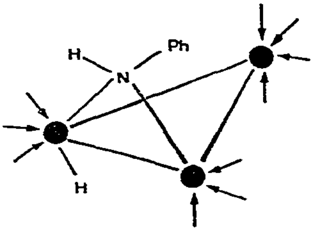
* Reactions between $Ru_3(CO)_{12}$ and $PhNO_2$ in basic aqueous methanol solutions yielded only the hydrides $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$.



[A]



[B]

pressure; for this compound we propose a structure similar to that of the compounds $H_2Ru_3(CO)_9E$ (E=S, Se, Te) and $H_2Ru_3(CO)_9R^{13-15}$.

$HRu_3(CO)_{10}HNPh$ (III), is presumably the first product of hydrogen abstraction from aniline; the two alternative structures of Fig. 1 (A, B) are proposed, in both of which the nitrogen atom is considered as a three-electron donor, and the hydrogen atom as a one-electron donor, and therefore the effective atomic number rule is conserved; in both these structures the nitrogen atom is in a tetrahedral-like environment as observed for $Fe_2(CO)_6(HN \cdot NCR_2)_2$ and $Fe_2(CO)_6(NHR)_2$[2], the latter being obtained only from azidobenzene, but not from $Fe_2(CO)_6(NR)_2$. Structure A is similar to the ones of the $HM_3(CO)_{10}SR$ compounds (M=Ru, Os)[11], whereas in structure B, the nitrogen atom must be optically active; to date we have not succeeded in detecting optical activity in CCl_4 solutions.

We have already evidenced that there is no correlation between the products obtained from nitrobenzene and aniline; by treating (I) with hydrogen, (IV) is obtained instead of (III). We have, however put in evidence the easy formation of trinuclear ruthenium compounds in which nitrene groups act as ligands; the very mild conditions in which the NR groups are formed, indicates as probable a catalytic formation of these units, in accordance with Dekker and Knox[2], as well as the formation of nitrene–metal intermediates with low-energy path, in accordance with Calderazzo's results[1].

Moreover, these compounds represent a new series of nitrogen–ruthenium compounds displaying a remarkable variety of structures.

The behaviour of $Os_3(CO)_{12}$, whose reactivity appears to be quite different from $Ru_3(CO)_{12}$, in these conditions, is by now under investigation.

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