INORGANIC CHEMISTRY

PREPARATION AND CERTAIN REACTIONS OF NITROSYLCARBONYL COMPLEXES $[\eta^5\text{-}C_5H_5M(CO)(NO)L]^{\oplus}BF_4^{\ominus}$ AND $[\eta^5\text{-}C_9H_7M(CO)(NO)L]^{\oplus}BF_4^{\ominus}$ $(M = Mn, Re, L = CO, PPh_3)$

N. E. Kolobova, I. A. Lobanova,
V. I. Zdanovich, and P. V. Petrovskii

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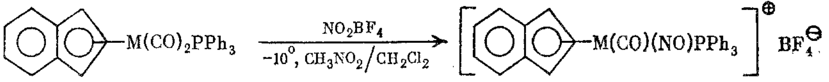
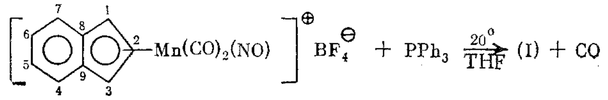
Recent years have seen a considerable increase in attention to cation nitrosylcarbonyl complexes of Group VII metals. In these complexes the carbonyl ligands are more reactive than in uncharged ones. It has been shown that replacement of the CO group by P-donor ligands in these compounds takes place readily, often at 20°C, and usually does not require UV radiation [1, 2]. The CO group also reacts with NH_3 and amines under mild conditions [3, 4]. Recently, particular attention has been paid to the reaction of reduction of the CO group in cation nitrosyl complexes, because the products of these reactions are models of intermediate compounds and catalysts of the Fischer–Tropsch synthesis [5-8].

Our aim is to synthesize new cation nitrosyl complexes of Mn and Re carbonyls with cyclopentadienyl and indenyl π ligands, and to investigate their reactions with PPh_3, halogens, and metal halides. The action of NO_2BF_4 on η^5-indenyldicarbonyltriphenylphosphinemanganese at −10° in a mixture of nitromethane and CH_2Cl_2 leads to formation (with a yield of 55%) of the nitrosyl complex of Mn (I)



M = Mn (I), Re (II).

The analogous complex of Re (II) was obtained by nitrosation of η^5-indenyldicarbonyltriphenylphosphinerhenium (III), which was hitherto unknown. We have developed a convenient method for its synthesis with a 70% yield by boiling $C_9H_7Re(CO)_3$ with PPh_3 in toluene. Under the ordinary conditions of preparation of phosphine complexes by UV radiation of $C_9H_7Re(CO)_3$ with PPh_3 for 30 h using a 1000-W Hg lamp, the yield of (III) is only 8%. We also obtained complex (I) with a ∼100% yield by the reaction of indenyldicarbonylnitrosylmanganese borofluoride with PPh_3



This reaction takes place readily in THF at 20°, similarly to the reaction with the cyclopentadienyl complex [2].

Complex (I) is a red crystalline substance, readily soluble in CH_2Cl_2, nitromethane, and acetone, sparingly soluble in THF, and insoluble in hexane. Cation [1] exhibits chirality as a result of the presence of four different ligands around the Mn atom; this was reflected in the NMR spectrum of ^{13}C of this compound. Whereas the NMR spectrum of ^{13}C of the initial indenyldicarbonylnitrosylmanganese cation contains only five different signals of the indenyl ligand at δ 86.57 (C^1, C^3), 97.4 (C^2), 126.20 and 134.91 (C^4, C^7 and C^5, C^6) and 111.91 ppm (C^8, C^9), the NMR spectrum of ^{13}C of (I) has eight signals from C atoms of the C_9H_7 fragment; this indicates the different magnetic environments of all the nine C atoms of the indenyl ligand in this compound (the two signals of the quaternary C atoms are not resolved).

We also investigated the reaction of cation nitrosyl complexes of Mn and Re with alkali-metal halides. It is known that the reaction of $[RC_5H_4Mn(CO)(NO)(L)]^{\oplus}X^{\ominus}$ ($L = CO, PPh_3$, $R = H, CH_3$) with KI and NaI leads to formation of $RC_5H_4Mn(NO)(L)I$; when L = CO the compounds are unstable, but when $L = PPh_3$ the complexes are stable in air [2, 9]. The reaction of $[C_9H_7Mn(CO)_2(NO)]^{\oplus}BF_4^{\ominus}$ with KI and NaCl was performed in different solvents (acetone, CH_3NO_2,

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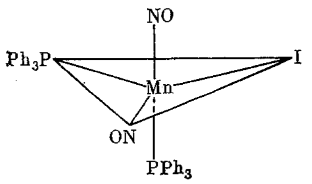

Fig. 1. Iodonitrosylbis(triphenylphosphine)manganese.

THF). Although a rapid reaction was observed in all cases, it seems that the complex formed is very unstable, like $C_5H_5Mn(CO)(NO)I$, and was not detected. The reaction of (I) with KI in THF takes place with detachment of the π ligand and formation of (IV) [10] with a 43% yield

$$\text{(I)} \xrightarrow[\text{THF, 20°}]{\text{KI}} \underset{\text{(IV)}}{Mn(NO)_2(PPh_3)_2I}$$

When the reaction was performed in CH_3CN or CH_2Cl_2, we also obtained complex (IV) with a 4% and 6% yield, respectively.

The NMR spectra of ^{13}C and ^{31}P of complex (IV) have interesting characteristics. It was found that (IV) has two spectrally different ligands PPh_3 and two different NO groups with νNO 1675 and 1723 cm^{-1}. The NMR spectrum of ^{13}C of complex (IV) exhibits two multiplets of C_6H_5 groups at the P atom, while the NMR spectrum of ^{31}P displays two singlets from ^{31}P nuclei with δ 51.74 and 43.16 ppm; the latter do not exhibit $^{31}P_1$—$^{31}P_2$ spin—spin splitting, even at −70°C. The data of the ^{13}C and ^{31}P NMR spectra of (IV) are attributable to the fact that one of the PPh_3 ligands of the complex is located in the equatorial plane, the other in the axial plane. The same is true as regards the NO groups (Fig. 1). Complexes of type $Mn(NO)_2(PPh_3)_2X$ (X = Br or CN) are also formed by the action of KBr and KCN on (I).

The reaction of $[C_5H_5Re(CO_2)(NO)]^{\oplus}BF_4^{\ominus}$ with KI has a different character. In this case, the π ligand is retained in the complex and we observe only replacement of one CO group by iodine with formation of (V)

$$[C_5H_5Re(CO)_2(NO)]^{\oplus}BF_4^{\ominus} \xrightarrow[\text{(or } I_2 \text{ in DMSO)}]{\text{KI}} \underset{\text{(V)}}{C_5H_5Re(CO)(NO)I}$$

The yield of (V) is 6-17%, depending on the solvent. However, when we react $[C_5H_5Re(CO)_2(NO)]^{\oplus}BF_4^{\ominus}$ with I_2 in DMSO (these conditions were used in [11]), the yield of (V) is 80%. In contrast to $C_5H_5Mn(CO)(NO)I$, compound (V) is stable in air and is a dark red crystalline substance, soluble in most organic solvents and insoluble in water. It is similar in physicochemical characteristics to $C_5H_5Re(CO)(NO)Br$, synthesized by a different method [12]. The IR spectrum (KBr) of (V) displays the frequencies of stretching vibrations of the NO group (1719 cm^{-1}) and the CO group (1985 cm^{-1}), and also absorption bands assigned to the C_5H_5 ring (837, 1004, 1420, 3115 cm^{-1}). The mass spectrum exhibits the molecular ion $C_5H_5{}^{187}Re(CO)(NO)I^+$ with m/z 437 (78.4%), the $C_5H_5{}^{187}Re(NO)I^+$ ion with m/z 409 (92.5%), and the $C_5H_5{}^{187}ReI$ ion with m/z 379 (100%). The PMR spectrum of (V) in $CDCl_3$ displays a singlet from protons of the C_5H_5 ring with δ 5.89 ppm.

EXPERIMENTAL

The operations were performed in an inert atmosphere. The IR spectra were obtained in UR-20 and Specord 71-IR spectrometers, the PMR spectra in a Perkin—Elmer R-12 device (60 MHz, internal standard HMDS), the ^{13}C and ^{31}P NMR spectra in a Bruker—HX-90 device; the chemical shifts of the ^{13}C NMR spectra are given with respect to TMS, the ^{31}P NMR spectra with respect to H_3PO_4. We used purified, absolute solvents, redistilled in Ar, Al_2O_3 (act. II), SiO_2 L 5/40 μ, and SiO_2 L 100/160 μ.

η^5-Indenyltriphenylphosphinecarbonylnitrosylmanganese Borofluoride (I). a) We mixed 0.73 g (2.13 mmoles) of $[C_9H_7Mn(CO)_2(NO)]^{\oplus}BF_4^{\ominus}$ [13] and 0.74 g (2.82 mmoles) of PPh_3 in 24 ml of THF at 20°C. An orange precipitate was deposited from the solution after 1-2 min. The reaction mixture was stirred for 1 h, then filtered; the precipitate was washed with ether. We obtained 1.22 g (99%) of (I); the mp was 100°C (with decomp.) (CH_2Cl_2—hexane). Found: C 57.93; H 3.93; Mn 9.43; P 5.33%. $C_{22}H_{22}BNF_4MnO_2P$. Calculated: C 58.26; H 3.81; Mn 9.53; P 5.37%. The IR spectrum (KBr, cm^{-1}) is as follows: 2041 (ν CO), 1791 (ν NO), 1438 and 1482 (PPh_3), 1030-1090 and (BF_4). The ^{13}C NMR spectrum (δ, ppm, CH_2Cl_2) is: 84.79, 86.57 (C^1, C^3), 99.54 (C^2), 126.14 and 124.91 (C^4, C^7 and C^5, C^6), 129.03 and 131.24 (C^5, C^6 and C^4, C^7), 109.57 (C^8, C^9).

b) To a solution of 0.26 g (0.53 mmole) of $C_9H_7Mn(CO)_2PPh_3$ [14] in a mixture of 53 ml CH_3NO_2 and 26 ml CH_2Cl_2 we added with stirring (−10°C) 0.12 g (0.90 mmole) NO_2BF_4; mixing was continued for another 1 h at 20°C. The solvent was removed in vacuum, the oil so obtained was washed twice with ether, and the residue was recrystallized from alcohol and then from a mixture of CH_2Cl_2 and hexane. We obtained 0.17 g (55%) of (I).

Nitrosation of $C_9H_7Re(CO)_2PPh_3$. To a solution of 0.13 g (0.21 mmole) of $C_9H_7Re(CO)_2PPh_3$ in 20 ml CH_3NO_2 and 10 ml CH_2Cl_2 we added with stirring (−15°C) 0.05 g (0.38 mmole) NO_2BF_4, mixing was continued for 1 h at 20°C, followed by evaporation. The oil so obtained was washed twice with ether and recrystallized from C_2H_5OH, then from a mixture of CH_2Cl_2 and hexane. We obtained 0.1 g (7%) of (II). The analytically pure substance was not obtained. The IR spectrum (KBr, ν, cm^{-1}) is as follows: 1070-1110 (BF_4), 1760 (NO), 2021 (CO).

η^5-Indenyldicarbonyltriphenylphosphinerhenium (III). a) A solution of 0.57 g (1.47 mmole) of $C_9H_7Re(CO)_3$ [13] and 0.66 g (2.52 mmole) of PPh_3 in 78 ml of toluene was boiled for 18 h. The solvent was removed in vacuum, and the residue was chromatographed on a column with Al_2O_3. We eluted $C_9H_7Re(CO)_2PPh_3$ with a mixture of petroleum ether and $CHCl_3$ (10:1). After repeated chromatography on a column with Al_2O_3 (the eluent was a 4:1 mixture of petroleum ether and $CHCl_3$) we obtained 0.63 g (69%) of (III); the mp was 200-201°C (from a mixture of CH_2Cl_2 and hexane). Found: C 56.28; H 3.79; Re 30.01; P 5.00%. $C_{29}H_{22}ReO_2P$. Calculated: C 56.20; H 3.55; Re 30.07; P 5.00%. The IR spectrum (KBR, ν, cm^{-1}) was as follows: 708 m, 758 m, 811 w, 826 w, 1109 m, 1345 m, 1449 m, 1492 m, 1878 s, 1950 s, 3060 w. The PMR spectrum (δ, ppm, $CDCl_3$) was as follows: 5.09, 5.49 (C_5H_3), 7.94 ($C_6H_4 + 3C_6H_5$). The mass spectrum (70 eV, ^{187}Re, m/z (rel. int., %)): M^+ 620 (98), $M^+ - 2CO$ 564 (96.6), $M^+ - 2CO - PPh_3$ 302 (3), PPh_3^+ 262 (9.5), C_9H_7 115 (19.4).

b) A solution of 0.22 g (0.57 mmole) of $C_9H_7Re(CO)_3$ and 0.17 g (0.65 mmole) of PPh_3 in a mixture of 30 ml of benzene and 15 ml of hexane was irradiated for 34 h. The reaction mixture was evaporated and the residue chromatographed on a column with Al_2O_3 (the eluent was a 1:1 mixture of benzene and petroleum ether). We obtained 0.03 (8%) of (III); it was identified from the IR spectrum (KBr) and TLC. Compound (III) is obtained with the same yield in THF.

Iododinitrosylbis(triphenylphosphine)manganese. A mixture of 0.7 g (1.21 mole) of (I) and 0.23 g (1.39 mmole) of KI in 37 ml THF was mixed for 84 h at 20°C. After residence for 10 days at 20°C the solvent was removed in vacuum and the residue was chromatographed on a column with Al_2O_3. We eluted the brown band with benzene; this gave 0.4 g (43%)* of $Mn(NO)_2(PPh_3)_2I$ (IV) with an mp of 167-168°C (with decomp.) (from a mixture of CH_2Cl_2 and petroleum ether). Found: C 56.45; H 3.96; I 16.62; N 3.88; Mn 7.33; P 8.03%; mol. mass 767 (vapor osmometer). $C_{36}H_{30}IN_2MnO_2P$. Calculated: C 56.41; H 3.92; I 16.57; N 3.66; Mn 7.17; P 8.09%; mol. mass 765.79. The IR spectrum (ν NO, cm^{-1}, in CH_2Cl_2) is as follows: 1717, 1673 (see [15]). The ^{13}C NMR spectrum (δ, ppm ($J_{^{13}C-^{31}P}$, Hz), in CH_2Cl_2 is: 134.62 (4.4) (C_o), 128.64 (4.4) (C_m), 130.89 (C_p), 132.55 (25) (C-P), 134.42 (4.4) (C_o), 128.45 (4.4) (C_m), 130.89 (C_p), 131.57 (25) (C-P). In acetonitrile the yield of (IV) is 4%; in CH_2Cl_2, 6%.

Bromodinitrosylbis(triphenylphosphine)manganese. A mixture of 0.1 g (0.17 mmole) of (I) and 0.03 g (0.25 mmole) of KBr in 8 ml of THF was mixed for 5.5 h at 20°C. The solvent was evaporated in vacuum and the residue extracted with toluene. The extract was evaporated and the residue washed several times with pentane. We obtained 0.03 g (24%) of $Mn(NO)_2(PPh_3)_2Br$. The IR spectrum (NO, ν, cm^{-1}, CH_2Cl_2) is as follows: 1715, 1670 (see [15]).

Cyanodinitrosylbis(triphenylphosphine)manganese. A mixture of 0.21 g (0.36 mmole) of (I) and 0.07 g (1.08 mmole) of KCN in 4 ml of alcohol was mixed for 15 min at 50-60°C. The solvent was evaporated in vacuum. From the residue, by preparative TLC on Al_2O_3 (eluent $CHCl_3$) we obtained 0.02 g (9%) of $Mn(NO)_2(PPh_3)_2CN$. The IR spectrum (ν NO, cm^{-1}, CH_2Cl_2) is: 1720, 1676 (see [15]).

Iodo-η^5-cyclopentadienylnitrosylcarbonylrhenium. a) A mixture of 1.41 g (3.33 mmole) of $[C_5H_5Re(CO)_2(NO)]^{\oplus}BF_4^{\ominus}$ [5] and 0.57 g (3.43 mmole) of KI in 55 ml THF was mixed for 34 h at 20°C. After residence for 7 days at 20°C the solvent was removed in vacuum and the residue was chromatographed on a column with SiO_2 (the eluent was a 1:1 mixture of ether and petroleum ether). We obtained 0.08 g (6%) of (V); the mp was 160-161°C (from a mixture of CH_2Cl_2 and hexane). Found: C 16.56; H 1.29; Re 42.60; I 29.09%. $C_6H_5ReNO_2I$. Calculated:

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*Here and below for compounds of type $Mn(NO)_2(PPh_3)_2X$ (X = I, Br, or CN) the yield was calculated on the assumption that 1 mole of product is obtained from 1 mole of the initial compound.

C 16.51; H 1.15; Re 42.70; I 29.10%. When acetone or CH_3NO_2 is used as the solvent, the yield of (V) is 9 and 17%, respectively.

b) To a solution of 0.44 g (1.04 mmole) of $[C_5H_5Re(CO)_2(NO)]^{\oplus}BF_4^{\ominus}$ in 11 ml of DMSO we added dropwise with stirring (20°C) a solution of 0.26 g (1.02 mmole) of I_2 in 8 ml of DMSO. The reaction mixture was mixed for 2 h, then poured into 30 ml of water. The precipitate so obtained was filtered and dried in vacuum above P_2O_5. After recrystallization from a mixture of CH_2Cl_2 and hexane we obtained 0.36 g (80%) of (V); it was identified from the IR spectrum and the melting point.

CONCLUSIONS

1. The authors have obtained new compounds η^5-$C_9H_7M(CO)(NO)(PPh_3)^{\oplus}BF_4$ (M = Mn or Re) by nitrosation of η^5-indenyldicarbonyltriphenylphosphine complexes of Mn and Re.

2. The reaction of $[C_9H_7Mn(CO)(NO)PPh_3]^{\oplus}BF_4^{\ominus}$ with KX (X = I, Br, or CN) takes place with detachment of the π ligand and formation of $Mn(NO)_2(PPh_3)_2X$. In the analogous reaction with KI or I_2, $[C_5H_5Re(CO)_2(NO)]^{\oplus}BF_4^{\ominus}$ forms a new π-complex $C_5H_5Re(CO)(NO)I$.

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