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SHORT COMMUNICATION

Reaction Behavior of Decacarbonyldimetalates(2-) (*M* = Cr and Mo) towards the Nitrosyl Carbonyls of Iron and Cobalt

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Dedicated to Professor Wolfgang Beck on the Occasion of his 85th Birthday

Abstract. The reaction of the nitrosyl carbonyl complexes $[Fe(NO)_2(CO)_2]$ and $[Co(NO)(CO)_3]$ with the decacarbonyldimetalates $[M_2(CO)_{10}]^{2-}$ (M = Cr and Mo) in THF as the solvent at room temperature was investigated. Thereby a substitution of one nitrosyl ligand towards carbon monoxide was observed in each case. Both reactions afforded the known metalate complexes $[Fe(NO)(CO)_3]^-$ and $[Co(CO)_4]^-$, respectively. These species were isolated as their corresponding PPN salts [PPN^+ = bis(triphenylphosphane)iminium cation] in nearly quantitative yields. The products were unambiguously identified by their IR spectroscopic and elemental analytic data as well as by their characteristic colors and melting points.

Introduction

Long time ago the reaction of $[Ni(CO)_4]$ with the decacarbonyldimetalates $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo and W; molar ratio Ni:M of 3:2) was reported.[1] Thereby the anionic heterometallic metal clusters $[Ni_3M_2(\mu\text{-}CO)_3(CO)_{13}]^{2-}$ as their corresponding PPN salts [PPN^+ = bis(triphenylphosphane)iminium] were obtained and the molecular structures determined by X-ray crystallography. These cluster compounds exhibit a trigonal bipyramidal metal core with three nickel atoms in the equatorial plane of the metal framework. The electron counting in the sense of the 18e rule affords in each case 76 valence electrons (VE) for these anionic clusters. Therefore, these molecules do not obey the 18e rule and can be regarded as "electron-rich", i.e., a metal cluster possessing a trigonal bipyramidal structure (with nine *M*–*M* bonds) should exhibit only 72 VE following the EAN rule.

For obvious reasons and in the context of the "Nitrosyl-Verschiebungssatz"[2] we wanted to check if the fragment $Ni(CO)_2$ in these molecules can be substituted by the isoelectronic fragment Co(NO)(CO) and $Fe(NO)_2$, respectively. This was the starting point of the therein described investigations. Therefore we studied the reaction of the decacarbonyldimetalates $[M_2(CO)_{10}]^{2-}$ (M = Cr and Mo) with the corresponding isoelectronic nitrosyl carbonyl complexes $[Co(NO)(CO)_3]$ and $[Fe(NO)_2(CO)_2]$, respectively, which are additionally isosterical to the nickel tetracarbonyl. Thereby our studies were performed using analogous conditions as described in the synthesis of the Ni_3M_2 clusters mentioned before. Last but not least there is an actual interest in nitrosyl complexes because they play a very important role in biochemical and photochemical processes. Therefore many investigations in the field of such compounds are in the focus of the current chemical research.[3]

Results and Discussion

The reaction of the salt $(PPN)_2[Mo_2(CO)_{10}]$ with $[Co(NO)(CO)_3]$ (molar ratio Co:Mo of 3:2) in THF at room temperature resulted quickly in a dark brown solution. After stirring for about 10 h the solvent was removed in vacuo. Thereby some unreacted $[Co(NO)(CO)_3]$ was found in the condensation trap (redbrown color of the condensed THF and characterization by IR spectroscopy). The remaining residue was recrystallized from dichloromethane / diethyl ether and afforded after further characterization, that in the light of the cobalt complex, a complete carbonylation to the tetracarbonylcobaltate (1-) has occurred [see Equation (1)].

$$[Co(NO)(CO)_3] + CO \rightarrow [Co(CO)_4]^- + NO \qquad (1)$$

After the reaction the tetracarbonylcobaltate(1-) was obtained as PPN salt as pale lime green crystals in nearly quantitative yield and unambiguously identified by the characteristic IR spectrum and the defined melting point. The compound $PPN[Co(CO)_4]$ exhibited in the IR spectrum a strong ν(CO) vibration at 1890 cm^{-1} (KBr) and a defined decomposition point at 183 °C.[4] The oxidation state of the cobalt, which is here in the starting material as well as in the product assigned to -I, because the nearly linear arranged *M*–NO fragment in $[Co(NO)(CO)_3]$ – corresponding to the found structural bonding parameters[5] – is to comprehend as a NO^+ ligand. Therefore, corresponding to the formally shown Equation (1), merely a ligand substitution process takes place. Since, at the moment, we do not have any hint at the fate of the changed NO – in a narrower sense it is a product in the formulated carbonylation reaction in Equation (1) – we cannot give an

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exact interpretation of this transformation. Till now we were unable to identify NO as a species of the gas phase: access of molecular oxygen (from the atmosphere in the air) to the reaction solution afforded no hints at the formation of NO_2 or other gaseous N-containing oxides respectively. Furthermore, NO could not be identified as a co-ligand in CO-containing side products of the reaction. So far the formulation in Equation (1) has only a formal character and is referenced only to the isolated cobalt species obtained in nearly quantitative yield in this reaction. To verify this observed reaction behavior, furthermore, we investigated the analogous reaction with the nitrosyl carbonyl complex of iron, $[Fe(NO)_2(CO)_2]$.

The reaction of the salt $(PPN)_2[Mo_2(CO)_{10}]$ with $[Fe(NO)_2(CO)_2]$ (molar ratio Fe:Mo of 3:2) in THF at room temperature under analogous conditions as described before afforded in this case a dark red solution. After stirring for 4 h the solvent was completely removed in vacuo. Thereby also some unreacted $[Fe(NO)_2(CO)_2]$ was found in the condensation trap (dark red color of the condensed THF and characterization by IR spectroscopy). The remaining residue was recrystallized from dichloromethane/diethyl ether and afforded also in this case, that in the light of the reaction described before a carbonylation of the dinitrosyl of iron to the tricarbonylnitrosylferrate(1-) has occurred [see Equation (2)].

$$[Fe(NO)_2(CO)_2] + CO \rightarrow [Fe(NO)(CO)_3]^- + NO \qquad (2)$$

The tricarbonylnitrosylferrate(1-) was isolated as PPN salt as bright yellow crystals in nearly quantitative yield and unambiguously identified by the characteristic IR spectrum and the defined melting point at 180 °C.[6] In light of the overall reaction and a eventually occurring redox process the above mentioned fact is valid like in the case of the reaction with the cobalt nitrosyl carbonyl. Also in the case of iron we do not have any hint at the fate of the nitric oxide. In the same way the process formulated in Equation (2) has only a formal character and is related only to the Fe-containing product of the reaction. By a further work-up of the remaining solutions unfortunately no defined hints at side-products could be gained. Often after removing the solvent, a red oil remained which afforded no hints at NO ligands by the use of IR spectroscopy. Therefore our results are manifested only by the identification of the formed carbonylation products in nearly quantitative yields during the equimolar transformation as formulated in the ligand exchange reaction corresponding to Equations (1) and (2). Generally, it should be mentioned, that the use of both decacarbonyldimetalates $[M_2(CO)_{10}]^{2-}$ (M = Cr or Mo) during these studies afforded similar results. In light of side products should be mentioned, that in all of these reaction attempts small amounts of the metal hexacarbonyls $[M(CO)_6]$ (M = Cr and Mo) in form of colorless crystals were found on the finger of the condensation trap during removing the THF of the corresponding reaction solutions.

Long time ago in the literature was already reported, that substitutions on $[Co(NO)(CO)_3]$ with P-donor ligands, e.g. with phosphanes, with exchange of one carbonyl occur resulting in the type of complex $[Co(NO)(CO)_2L]$ (L = phosphanes).[7] The ligand NO^+ as well as the carbonyl ligand represent the strongest π acceptor ligands and they show only little differences in their π acidic behavior. However in most cases the ligand NO^+ is evaluated as a stronger π acceptor than the CO ligand.[8] Thus $[Fe(NO)_2(PPh_3)_2]$ is formed from the iron nitrosyl carbonyl in the presence of an appropriate amount of the phosphane.[9] Even multinuclear complexes, e.g. Roussin's red salt esters (RRE), were obtained from $[Fe(NO)_2(CO)_2]$ by reaction with the corresponding thiolato ligands, whereas also in these cases only the both carbonyl ligands were substituted.[10]

These facts were the basis of our originally aspired synthetic efforts, i.e., to set a fragment Co(NO) instead of a Ni(CO) fragment (in each case 12 VE) in the above mentioned metal cluster structures. Nevertheless it seems that the reactivity of the nitrosyl carbonyls towards CO described therein have obviously less to do with the former reactions including substitutions with phosphane ligands. Partially in the literature it was reported that carbonylmetalates can serve as CO transfer reagents. For example, complexes $[Ni(PPh_3)_2X_2]$ (X = halide) reacted with carbonylmetalates of iron, whereas carbonyl compounds with the formula $[Ni(PPh_3)_2(CO)_2)]$ resulted.[11] However the latter reaction is to discuss as a redox process since the metalates serve additionally as reducing agents. Thus the general CO transfer observed during our studies described therein seems to be not so unusually. Because there is no evidence on the fate of the nitric oxide during the described transformation we can not give some remarks on the mechanism of these reactions. In light of the obvious maintenance of the oxidation state of the central atoms in the starting materials as well as in the identified products, it seems unlikely that during these nearly quantitative occurring reactions nitric oxide in the molecular form is released. Therefore it could obviously also not be identified in the gaseous phase by us.

Conclusions

The reaction of the nitrosyl carbonyl complexes of cobalt and iron, respectively, with the decacarbonyldimetalates $[M_2(CO)_{10}]^{2-}$ (M = Cr and Mo) resulted in each case in a clean substitution of a NO towards a CO ligand, whereas in nearly quantitative yields the anionic complexes $[Co(CO)_4]^-$ and $[Fe(NO)(CO)_3]^-$ respectively were obtained. Till now we have no hints at NO-containing side-products, thus no statement on the mechanism of the reaction can be given. For a better understanding of this kind of reactivity a further search for other side-products is necessarily. To this purpose in our laboratory further studies on the reaction behavior of carbonylmetalates containing other central atoms towards the nitrosyl carbonyl complexes mentioned therein are planned in the near future.

Experimental Section

General: All preparative work was carried out in a dry nitrogen atmosphere using standard Schlenk techniques. Chemicals were purchased from Sigma/Aldrich and used as received. The compounds $[Co(NO)(CO)_3]$,[12] $[Fe(NO)_2(CO)_2]$,[13] and $(PPN)_2[M_2(CO)_{10}]$ (M = Cr and Mo)[14] were prepared according to literature procedures. IR spectra were recorded from solids with a JASCO FT/IR-460 plus spectrometer equipped with an ATR unit. Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, with a Heraeus Elementar Vario EL instrument. Melting points were determined in sealed capillaries in a nitrogen atmosphere and are uncorrected.

Reaction of $(PPN)_2[Mo_2(CO)_{10}]$ with $[Co(NO)(CO)_3]$: $(PPN)_2[Mo_2(CO)_{10}]$ (1550 mg, 1.00 mmol) was suspended in THF (40 mL) at room temperature with stirring and $[Co(NO)(CO)_3]$ (519 mg, 3.00 mmol) was added by syringe. The mixture was stirred for 10 h. The resulting dark brown solution was evaporated to dryness in vacuo. *Caution:* During this procedure the excess of the volatile and toxic $[Co(NO)(CO)_3]$ was distilled in the condensation trap! The remaining residue was crystallized from dichloromethane/diethyl ether (5:35 mL) affording $PPN[Co(CO)_4]$ as pale lime green crystals. The solid was filtered off, washed with a small amount of diethyl ether and dried in vacuo. Yield: 680 mg (96 %, related on 1 equivalent of nitrosyl carbonyl). M.p. 182–186 °C (dec.). $C_{40}H_{30}CoNO_4P_2$ (709.56); C 67.48 (calcd. 67.71); H 4.21 (4.26); N 1.89 (1.97) %. **IR** (CO, KBr): $\tilde{\nu}$ = 1890 vs cm^{-1}.

Reaction of $(PPN)_2[Mo_2(CO)_{10}]$ with $[Fe(NO)_2(CO)_2]$: $(PPN)_2[Mo_2(CO)_{10}]$ (1550 mg, 1.00 mmol) was suspended in THF (40 mL) at room temperature with stirring and $[Fe(NO)_2(CO)_2]$ (516 mg, 3.00 mmol) was added by syringe. The mixture was stirred for 4 h. The resulting red brown solution was evaporated to dryness in vacuo. *Caution:* During this procedure the excess of the volatile and toxic $[Fe(NO)_2(CO)_2]$ was distilled in the condensation trap! The remaining residue was crystallized from dichloromethane / diethyl ether (5:35 mL) affording $PPN[Fe(NO)(CO)_3]$ as bright yellow crystals. The solid was filtered off, washed with a small amount of diethyl ether and dried in vacuo. Yield: 675 mg (95 %, related on 1 equivalent of nitrosyl carbonyl). M.p. 180–183 °C (dec.). $C_{39}H_{30}FeN_2O_4P_2$ (708.47); C 65.91 (calcd. 66.12); H 4.35 (4.27); N 4.08 (3.95) %. **IR** (CO, KBr): $\tilde{\nu}$ = 1982 s, 1875 vs. (br) cm^{-1}. **IR** (NO, KBr): $\tilde{\nu}$ = 1650 vs cm^{-1}.

Similar results were obtained during theses preparations using the compound $(PPN)_2[Cr_2(CO)_{10}]$ instead of the analogous molybdenum species as the carbonylation agent.

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Keywords: Nitrosyl complexes; Iron; Cobalt; Carbonyl metalates

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