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Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF MANGANESE AND RHENIUM TRICARBONYL COMPLEXES WITH (*O,O,O*)-DONOR LIGANDS

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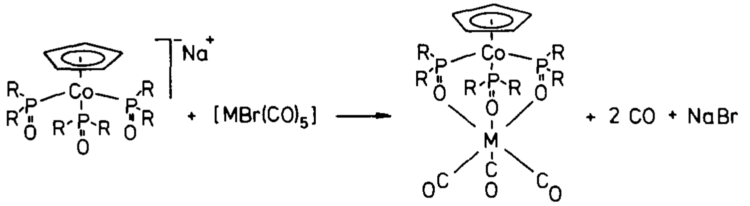
Summary

Complexes of the type $[(C_5H_5)Co\{P(O)R_2\}_3]^-$, R = OCH_3, OC_2H_5, react as tridentate oxygen ligands L^- with $[MBr(CO)_5]$, M = Mn, Re, in hexane or tetrahydrofuran to give the tricarbonyl derivatives $[LM(CO)_3]$. The slightly volatile yellow crystalline compounds have been characterized by elemental analysis, ^{1}H NMR, IR and mass spectra. The low CO stretching frequencies indicate that the ligands L^- are good π-donor ligands.

We previously reported a variety of neutral and cationic metal complexes $ML_2^{(n-2)+}$ with L^- = $[(C_5H_5)Co\{P(O)R_2\}_3]^-$ acting as oxygen tripod ligands [1]. Nearly all main group and transition metal ions M_{aq}^{n+}, n = 2, 3, 4, seem to react readily with ligands of type L^- to form ML_2 complexes. We have now discovered that such oxygen ligands also form surprisingly stable low valent chromium, molybdenum, and tungsten carbonyl complexes [2]. Since metal carbonyl derivatives containing oxygen donor ligands are normally rather labile, and often thermally unstable, we decided to investigate the transition metal carbonyl chemistry of the ligand type L^-. We describe below the synthesis and characterization of manganese and rhenium tricarbonyl derivatives of the oxygen ligands $[(C_5H_5)Co\{P(O)R_2\}_3]^-$, R = OCH_3, OC_2H_5.

Results and discussion

Manganese pentacarbonyl bromide reacts with the oxygen tripod ligands L^- = $[(C_5H_5)Co\{P(O)R_2\}_3]^-$, R = OCH_3, OC_2H_5, in hexane to yield the



(1)

(R = OCH_3, OC_2H_5; M = Mn, Re)

tricarbonyl complexes [$LMn(CO)_3$] (eq. 1, M = Mn). Ligand substitution reactions involving [$MnX(CO)_5$] are characterized by facile carbon monoxide substitution *cis* to the halogen X [3]. The replacements of the first and second CO ligands by simple two electron donors L′ often occur with similar rate constants, and the complexes [$MnXL'_2(CO)_3$] initially show facial coordination geometry. We suspect that a similar reaction sequence is followed with our oxygen ligands L^-. The sodium salt of the ligand L^- = [$(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3$]$^-$ is readily soluble in hexane. Molecular weight determinations show NaL to exist as trimers in non coordinating solvents, and it could well be that fragments like $MnBr(CO)_4$ or $MnBr(CO)_3$ are coordinated to such trimers. The appearance of one of the intermediates can be monitored by its IR spectrum, but we have been unable to isolate and characterize it. The formation of sodium bromide obviously is not involved in the rate-determining step, and this is of interest since previously we had always found that L^- was a good nucleophile only when the complex formation reactions were carried out in water or organic solvents which solvate the sodium ions effectively. With manganese pentacarbonyl bromide in refluxing hexane the reaction is complete after 15 to 120 min depending on L^-.

The complexes [$LMn(CO)_3$] are bright yellow solids, which can be handled in air for short periods of time. In solution they are easily oxidized to give manganese(II) compounds and the ligand L^- is recovered quantitatively as [MnL_2], which was identified by comparison with an authentic sample [4]. We found that two alternative routes starting from [$Mn(OClO_3)(CO)_5$] and [$(C_6H_6)Mn(CO)_3$]PF_6 also lead to [$LMn(CO)_3$]. The reaction with the perchlorate complex is a multistep process like that with manganese pentacarbonyl bromide, whereas the displacement of benzene in [$(C_6H_6)Mn(CO)_3$]$^+$ by L^- seems to be a clean reaction without any detectable intermediates in the ^1H NMR and IR spectra.

The IR spectra of the compounds $LMn(CO)_3$ show two strong bands in the $\nu(CO)$ region in addition to the characteristic pattern of the ligands L^- in the fingerprint region [4]. The P=O stretching frequency occurs at 1125 cm^{-1}, 45 cm^{-1} lower than in the sodium salts NaL. This shift to longer wavelengths corresponds to a substantial reduction of the P=O bond order upon coordination to the manganese tricarbonyl fragment. The consequent increase in electron density at the manganese centre is reflected in the low $\nu(CO)$ frequencies. The metal-to-CO back bonding is even more pronounced in the homologous rhenium complex $LRe(CO)_3$, and is discussed in more detail in the next paragraph. The ^1H NMR spectra of $LMn(CO)_3$ are, apart from minor chemical shift differences, identical with the spectra of diamagnetic ML_2 complexes

[4—6]. This proves that the ligands L^- have remained intact and that their C_{3v} symmetry is preserved in the manganese tricarbonyl derivatives. The mass spectra of $LMn(CO)_3$ show the ions $M^+ - CO$ at $m/e = 562$ ($R = OCH_3$) and $M^+ - 3CO$ at $m/e = 590$ ($R = OC_2H_5$) as the heaviest fragments. The ions LMn^+ form the base peak in both cases. The fragmentation of the ligand is involved but follows the same pattern as in other metal complexes of L^-.

The rhenium tricarbonyl compound $[LRe(CO)_3]$, $L^- = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$, is prepared from rhenium pentacarbonyl bromide and NaL in boiling anhydrous tetrahydrofuran. It is important to note that $[ReBr(THF)_2(CO)_3]$ in THF cannot be used as starting material. Although this compound has often been used successfully as a labile rhenium tricarbonyl source in reactions where $[ReBr(CO)_5]$ proved unreactive [7], we observed no formation of $[LRe(CO)_3]$ when we first synthesized $[ReBr(THF)_2(CO)_3]$ from $[ReBr(CO)_5]$ in tetrahydrofuran and then refluxed NaL with $[ReBr(THF)_2(CO)_3]$ in THF for two days. In keeping with this surprising observation we did not detect $[ReBr(THF)_2(CO)_3]$ as an intermediate during the reaction of NaL with $[ReBr(CO)_5]$ in tetrahydrofuran. At present we cannot offer an easy explanation for this. The formation of $[LRe(CO)_3]$ is complete after 24 h, and no other carbonyl complexes are detected in the final IR spectrum. Recrystallization from hexane yields $[LRe(CO)_3]$ as yellow needles. The compound is completely air stable and can be sublimed at 100°C in high vacuum. Its mass spectrum shows the molecular ion at $m/e = 806$ (^{187}Re) and this, together with the elemental analysis, confirms the composition $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3Re(CO)_3]$. The ^1H NMR spectrum of $[LRe(CO)_3]$ shows the same characteristic pattern as NaL [5] and $LMn(CO)_3$ (see above), which is in accord with the anticipated C_{3v} symmetry of both L^- and $[LRe(CO)_3]$. The CO stretching frequencies of $[LRe(CO)_3]$ and some comparable other rhenium tricarbonyl complexes are given in Table 1.

TABLE 1

ν(CO) FREQUENCIES OF *fac*-$Re(CO)_3$ COMPLEXES CONTAINING ANIONIC LIGANDS

$[(C_5H_5)Re(CO)_3]$	2034, 1941 (C_6H_{12})	[11]
$[(C_5Me_5)Re(CO)_3]$	2016, 1925 (C_6H_{12})	[11]
$[\{Re(OH)(CO)_3\}_4]$	2021, 1919 (THF)	[12]
$[ReCl_3(CO)_3]^{2-}$	2000, 1900 (fluorolube)	[13]
$[HB(3,5\text{-}Me_2pz)_3Re(CO)_3]$ [a]	2040, 1890 (KBr)	[9b]
$LRe(CO)_3$	2017, 1896 (C_6H_{12})	
	2015, 1878 (KBr)	

[a] pz = pyrazolyl.

It is seen that the oxygen tripod L^- induces more metal-to-CO back bonding than all the other ligands. It shifts the ν(CO) bands to lower wave numbers about as much as three chloride ligands, despite the fact that it carries only one negative charge. The strong electron-donating properties of L^- are surprising at first sight, since we have characterized L^- unequivocally as a very weak ligand in the spectrochemical series [6]. The observations can be accounted for satisfactorily, however by assuming that L^- is a strong π-donor ligand. A qualitative MO scheme of an octahedral transition metal complex shows that increasing π-donor capability of the ligands is paralleled by decreasing ligand field strength [8].

Concluding remarks

The oxygen tripod ligands L^- are formally equivalent to a cyclopentadienyl unit in the sense that they are also $6e^-$-ligands occupying three facial positions in octahedral or pseudooctahedral metal complexes. We are currently exploring the organometallic chemistry of $[LMn(CO)_3]$ and $[LRe(CO)_3]$ to see whether this analogy is a useful one. The photochemically accessible dicarbonyl fragments $[LM(CO)_2]$ e.g. could be regarded is isolobal to $[(C_5H_5)M(CO)_2]$, $[(C_5Me_5)M(CO)_2]$, and $[(HBpz_3)M(CO)_2]$ [9], M = Mn, Re. In this respect it will be interesting to compare the chemistry of these fragments which in turn are isolobal to CH_2 [10].

Experimental

The complexes $[MnBr(CO)_5]$ [14], $[ReBr(CO)_5]$ [7] and NaL [5] were prepared as described in the literature. All reactions were carried out under nitrogen, and in N_2-degassed dry solvents. IR and ^{1}H NMR spectra were recorded using PE 567, PE 580, Jeol C60HL, and Varian XL 100 spectrometers, respectively. Mass spectra were measured on a Varian MAT CH5 spectrometer (electron impact, 70 eV, 30—80°C).

$[(C_5H_5)Co\{P(O)R_2\}_3Mn(CO)_3]$, R = OCH_3, OC_2H_5 ($[LMn(CO)_3]$). A solution of 550 mg (2.0 mmol) $[MnBr(CO)_5]$ and 2.2 mmol NaL in hexane was heated under reflux for 15 min (R = OC_2H_5) or 2 h (R = OCH_3). The solvent was evaporated and the residue was dissolved in a minimum amount of warm methanol (35°C). Some insoluble residues were quickly filtered off and the manganese tricarbonyl complex $[LMn(CO)_3]$ was precipitated out with a little deionized water. The product was filtered, washed with water and cold methanol, and dried in vacuo. Yield 1.5—1.7 mmol (ca. 80%) yellow crystals. The compounds must be stored under an inert atmosphere. $[LMn(CO)_3]$, R = OC_2H_5, is freely soluble, the corresponding R = OCH_3 compound is only slightly soluble in saturated hydrocarbons. Found (R = OCH_3): C, 28.81; H, 4.12. $C_{14}H_{23}CoMnO_{12}P_3$ calcd.: C, 28.50; H, 3.93%; found (R = OC_2H_5): C, 35.91; H, 5.44. $C_{20}H_{35}CoMnO_{12}P_3$ calcd.: C, 35.63; H, 5.23%. ^{1}H NMR ($CDCl_3$, R = OCH_3): δ(ppm) 3.7 (virt. q, 18H, OCH_3); 5.0 (s, 5H, C_5H_5). ^{1}H NMR ($CDCl_3$, R = OC_2H_5): δ(ppm) 1.3 (t, ^3J(HCCH) 7 Hz, 18H, CH_3); 4.1 (m, 12H, OCH_2); 4.9 (s, 5H, C_5H_5). IR: 2033 st, 1920 st (ν(CO), pentane); 1125 cm^{-1} (ν(P=O), KBr).

$[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3Re(CO)_3]$ ($[LRe(CO)_3]$). A solution of 558 mg (1.00 mmol) anhydrous $Na[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]$ (NaL) and 406 mg (1.00 mmol) $[ReBr(CO)_5]$ in 15 ml dry tetrahydrofuran was heated to reflux. The vessel was flushed with nitrogen from time to time and the formation of $[LRe(CO)_3]$ was monitored by IR. The reaction was stopped after 24 h, the turbid reaction mixture evaporated to dryness, and the solid residue was chromatographed on silica with pentane/diethyl ether 1/1. A bright yellow band was collected. The residue after evaporation was recrystallized from hexane at −20°C to give 710 mg (0.88 mmol, 88%) $[LRe(CO)_3]$ as air stable yellow needles. It sublimes at ca. 100°C in high vacuum. M.p. 198—200°C.

Found: C, 29.68; H, 4.40. $C_{20}H_{35}CoO_{12}P_3Re$ calcd.: C, 29.82; H, 4.38%. ^1H NMR ($CDCl_3$): δ(ppm) 1.3 (t, ^3J(HCCH) 7 Hz, 18H, CH_3); 4.3 (m, 12H, OCH_2); 4.9 (s, 5H, C_5H_5). IR: 2017 st, 1896 st (ν(CO), C_6H_{12}); 1120 st cm^{-1} (ν(P=O), KBr).

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