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LIGAND EXCHANGE AND LIGAND MIGRATION REACTIONS INVOLVING DICYCLOPENTADIENYLNIOBIUM(III) CARBONYL DERIVATIVES

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Summary

The methylniobocene carbonyl $(C_5H_5)_2Nb(CH_3)(CO)$ shows an unexpected lack of reactivity with respect to ligand migration. Whereas $(C_5H_5)_2V(CH_3)$ has been reported to react with CO to yield the acetyl derivative $(C_5H_5)_2V(OCCH_3)(CO)$ immediately, we find that the niobocene analogue $(C_5H_5)_2Nb(CH_3)$ reacts with CO only to regenerate $(C_5H_5)_2Nb(CH_3)(CO)$, from which it was obtained by photolysis. This resistance of the methylniobocene carbonyl derivative towards ligand migration is interpreted in terms of the bonding properties of the acetyl intermediate $(C_5H_5)_2Nb(OCCH_3)$.

Introduction

Unusual examples of ligand migrations to a CO ligand, which lead to novel η^2-acyl products or, when hydride is the migrating ligand, to multiple hydride transfer to the CO ligand group, have recently been reported to occur with dicyclopentadienyl-Group IV transition metal derivatives [1—4]. The high oxygen affinity of these metals, which may make a major contribution to the driving force of these unusual ligand migration reactions must, at the same time, preclude the possibility of catalytic reaction cycles, by which, e.g., a reduction of CO by dihydrogen could be accomplished; the transition metal—oxygen bonds stabilizing the products of these ligand migrations are not likely to be cleaved by reaction with CO or H_2 to regenerate the original, reduced metal species. It can be assumed that catalytic reaction cycles are more likely to be encountered with related Group V or VI transition metal compounds, for which the tendency toward formation of thermodynamically inert metal—oxygen bonds is not so pronounced as with Group IV transition metals.

In an attempt to study ligand migration reactions with related niobium derivatives, Labinger, Wong and Scheidt [5], recently observed that the niobocene carbonyl hydride $(C_5H_5)_2Nb(CO)H$ does not yield any products derived from a metal-to-CO hydride migration until a total breakdown of the sandwich structure was induced at temperatures above 140°C. In order to establish the factors responsible for this lack of reactivity, and bearing in mind the observation that metal-to-CO migrations proceed more easily with a methyl than with a hydride ligand group, we have undertaken a study of the reaction of the methylniobocene carbonyl derivative $(C_5H_5)_2Nb(CH_3)(CO)$ and some related compounds. We discuss below our observations on these systems, and their relevance to the limitations of catalytical reduction of CO.

Results and discussion

Methyldicyclopentadienylniobium carbonyl $(C_5H_5)_2Nb(CH_3)(CO)$ was prepared in 50—60% yield by reduction of the chloromethyl derivative $(C_5H_5)_2Nb(CH_3)Cl$ in the presence of CO *. It is obtained, after sublimation at 50—60°C in vacuo, as a green material with spectral properties in agreement with those reported by Fredericks and Thomas [6]. The compound was subjected to CO pressure up to 200 bar at temperatures between 20 and 50°C in toluene solution for 16 h. After cooling to room temperature and release of CO pressure, these solutions did not show any CO absorption bands in the IR in addition to that of $(C_5H_5)_2Nb(CH_3)(CO)$ at 1890 cm^{-1}. The mass spectrum of the residue obtained after removal of solvent did not give indication of the presence of the acetyl derivative $(C_5H_5)_2Nb(OCCH_3)(CO)$; unchanged $(C_5H_5)_2(CH_3)(CO)$ was recovered from this residue by sublimation in essentially quantitative yield.

Reaction of a carbonyl complex with a carbanionic alkyl compound, such as methyllithium, has been reported as an alternative route to acetylmetal derivatives [7,8]. This nucleophilic attack is especially favoured if the carbonyl complex carries a cationic charge. Accordingly, we have treated the cationic niobocene dicarbonyl complex $(C_5H_5)_2Nb(CO)_2^+$ [9], with stoichiometric amounts of CH_3Li. Upon addition of one equivalent of CH_3Li in diethyl ether to a suspension of yellow $(C_5H_5)_2Nb(CO)_2(BF_4)$ in tetrahydrofuran (THF) at room temperature, a dark green solution is formed the IR spectrum of which contains only one CO absorption band at 1890 cm^{-1}, assignable to the methyl carbonyl $(C_5H_5)_2Nb(CO)(CH_3)$.

This compound, $(C_5H_5)_2Nb(CH_3)(CO)$, probably arises from the reaction of CH_3Li with $(C_5H_5)_2Nb(CO)_2^+$ by the following sequence: attack of a methyl anion at one of the carbonyl groups would form the acetyl derivative $(C_5H_5)_2Nb(OCCH_3)(CO)$. This intermediate might then, by loss of CO and retro-migration of the methyl ligand to the metal centre, yield the methyl carbonyl $(C_5H_5)_2Nb(CH_3)(CO)$ as a stable product. Such a reaction sequence would imply that a ligand migration equilibrium is rapidly established and lies altogether on the side of the carbonyl rather than the acyl derivative, even with CH_3 as migrating ligand.

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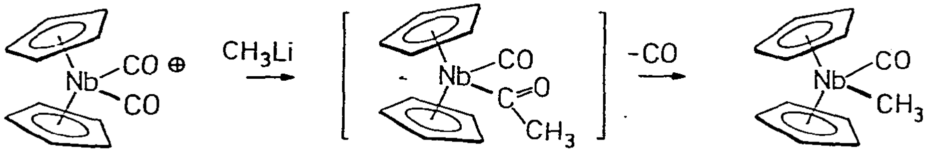
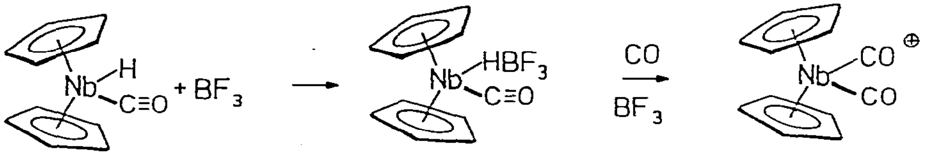
* A number of other methyl-ligand derivatives $(C_5H_5)_2Nb(CH_3)L$ (L = $P(OCH_3)_3$, $P(C_2H_5)_3$, C_2H_4) can also be obtained by this method (see experimental part).



Alternatively, however, CH_3Li might attack at the metal centre directly, with displacement of one of the CO ligands. If this were the case, no clear statements concerning the CH_3 migration reaction could be derived from these observations. We feel, that such a direct ligand substitution process is less likely than a nucleophilic attack at a CO ligand, since the dicarbonyl cation complex did not show any other indication of substitutional lability.

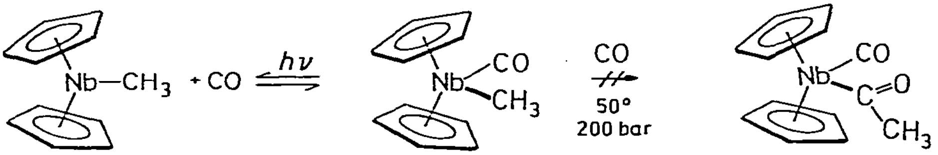
Since a ligand migration reaction such as the transformation of $(C_5H_5)_2Nb(CH_3)(CO)$ into $(C_5H_5)_2Nb(OCCH_3)$ might be susceptible to an assistance by Lewis acids [10], we have further investigated the effects of Lewis acids such as BF_3, on these reaction systems. When BF_3 is added to a blue-violet solution of the carbonyl hydride $(C_5H_5)_2Nb(CO)H$ in toluene, a red-violet precipitate is formed. The CO absorption of this compound is shifted from 1900 cm^{-1} in $(C_5H_5)_2Nb(CO)H$ to 1930 cm^{-1}. The solid compound obtained in this manner appears to be stable under reaction conditions employed. In the presence of an excess of BF_3, however, CO is taken up to form the dicarbonyl cation $(C_5H_5)_2Nb(CO)_2^+$. An essentially identical reaction sequence is observed when $(C_5H_5)_2Nb(CH_3)(CO)$ rather than $(C_5H_5)_2Nb(CO)H$ is treated with BF_3 and CO. We interpret the formation of the insolubleBF_3 adducts as an indication for the production of at least partially ionic derivatives containing a complex borate anion. This assignment is supported by the similarity of the visible and IR absorptions of these products to those of the tetrafluoroborate derivative $(C_5H_5)_2Nb(CO)(BF_4)$ described earlier [9].



A similar tendency of the Lewis acid triethylaluminum to undergo attachment to the hydride ligand of $(C_5H_5)_2Nb(CO)H$, to form $(C_5H_5)_2Nb(CO)(HAlEt_3)$, has been observed by Tebbe [11]. Such a coordination by a potential migrating ligand would tend to suppress rather than enhance a ligand migration process. Whether other Lewis acids with a coordination preference for the "hard" carbonyl oxygen atom (see e.g. ref. 12) can, by electrophilic assistance, induce a ligand migration onto a CO ligand group remains to be established.

Conclusions

The absence of any detectable tendency of the methylniobocene carbonyl to form an acetyl product by reaction with CO is puzzling. To the best of our knowledge, there is no other transition metal *cis*-methyl carbonyl derivative which shows a comparable reluctance to undergo ligand migration reactions. The analogous vanadium derivative is so reactive with respect to CO insertion that $(C_5H_5)_2V(CH_3)$ takes up CO to yield the acetyl compound $(C_5H_5)_2V(OCCH_3)(CO)$ without any detectable accumulation of $(C_5H_5)_2V(CH_3)(CO)$ [13] which apparently reacts with CO faster than it is formed from $(C_5H_5)_2V(CH_3)$ and CO. In order to provide observations strictly comparable to those for the vanadocene system, we have prepared $(C_5H_5)_2Nb(CH_3)$ by photolysis of $(C_5H_5)_2Nb(CH_3)(CO)$ and studied its reactions with CO; green solutions of $(C_5H_5)_2Nb(CH_3)(CO)$ in toluene became an intense blue when irradiated at temperatures of about —78° C in vacuo. The dark blue, paramagnetic solution obtained after loss of almost 1 mmol CO/Nb is free of any significant IR absorption bands in the CO absorption region. We conclude that these solutions contain the species $(C_5H_5)_2Nb(CH_3)$ which, like its vanadium analogue $(C_5H_5)_2V(CH_3)$ [14], is present in a high-spin d^2 configuration *. Admission of CO to $(C_5H_5)_2Nb(CH_3)$ regenerates the methylniobocene carbonyl derivative exclusively in high yield. This observation on the otherwise strictly analogous methyl-niobocene and -vanadocene reaction systems highlights the difference in their tendency to undergo ligand migrations.



Our results do not provide the basis for a decision on whether this unexpected difference in reactivity is of thermodynamic or kinetic origin, i.e. whether (i) the ligand migration equilibrium is rapidly established but entirely displaced towards the reactants $(C_5H_5)_2Nb(CH_3)(CO)$ and CO, or (ii) this ligand migration process is energetically favourable but kinetically hindered. Irrespective of this question, however, it is apparent that the primary ligand migration intermediate, i.e. the acetyl derivative $(C_5H_5)_2Nb(OCCH_3)$, must be energetically more unfavourable compared with $(C_5H_5)_2Nb(CH_3)(CO)$ than is $(C_5H_5)_2V(OCCH_3)$ compared with $(C_5H_5)_2V(CH_3)(CO)$. All the $(C_5H_5)_2Nb(CO)X$ compounds studied so far are at least as stable with respect to loss of CO as their vanadocene counterparts. Accordingly, complex formation between the acetyl species and CO cannot be the origin of greater stabilization for $(C_5H_5)_2V(OCCH_3)(CO)$ than for $(C_5H_5)_2Nb(OCCH_3)(CO)$. Any thermodynamic advantage of the acetylvanadocene carbonyl over its niobocene analogue must arise, therefore, from a lower relative energy of the vanadocene acetyl intermediate compared to its niobocene analogue.

The same conclusion is reached by kinetic considerations: the energy of the transition state which determines the rate of a methyl migration reaction is,

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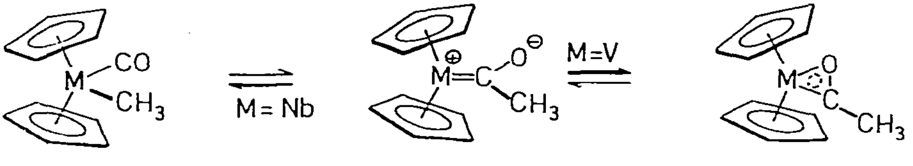
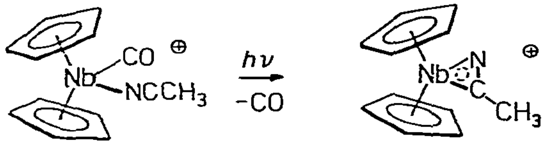
* Solutions of the methyl compound $(C_5H_5)_2Nb(CH_3)$ appear to be fairly stable at room temperature. At slightly elevated temperatures (40—50° C) they become dark brown, and binuclear species such as dimeric niobocene are revealed by the mass spectra of the solid residue. This observation and the formation of $(C_5H_5)_2Nb(CO)H$ upon admission of CO to these solutions indicate that the methyl compound possibly decomposes via a rearrangement to a methylene hydride, $(C_5H_5)_2Nb(CH_3) \rightarrow (C_5H_5)_2Nb(CH_2)H$, analogous to that observed by Cooper and Green [15] for the isoelectronic methylmolybdenocene cation $(C_5H_5)_2Mo(CH_3)^+$.

according to an extended study by Berke and Hoffmann [10], expected in close vicinity to that of the acetyl intermediate.

In considering the factors which contribute to the thermodynamically as well as kinetically unfavourable rise in energy associated with the conversion of the methylniobocene carbonyl to the acetyl derivative, account must be taken of the fact that in the reaction intermediate considered here, an acetyl ligand is attached to a metal centre with non-bonding *d* electrons of very low ionisation energy for which no other π-acceptor ligand is competing. It must be expected, therefore, that almost complete polarization toward an anionic oxicarbene ligand structure would occur. In accord with this assumption, we find that an extended Hückel molecular orbital analysis of species of this kind invariably yields a negative charge of more than one charge unit for the $OCCH_3$ ligand group [16]. Such a ground-state charge transfer from the metal centre to an acetyl ligand is expected to arise whenever the metal fragment contains non-bonding electrons at an energy higher than about —8 eV. It is apparent that such a charge accumulation on the acetyl oxygen would gain substantial stabilization from interaction with an electrophilic centre, either of a Lewis acid present in the reaction system, or intramolecularly by coordination of the acetyl oxygen atom to the metal centre in an η^2-acetyl structure. The formation of such a bicoordinate acetyl derivative, however, appears to be crucially dependent, as indicated by a molecular orbital analysis [16], on the energy separation between the acetyl fragment orbital containing the oxygen lone pairs and the lowest empty metal-centred orbital which could act as an acceptor orbital in forming the oxygen—metal bond. The size of this energy separation thus appears to be the decisive parameter which discriminates between a rapid ligand migration as in $(C_5H_5)_2V(CH_3)(CO)$ and an impossible one as in $(C_5H_5)_2Nb(CH_3)(CO)$. The more positive intrinsic valence state ionisation energy of a niobium metal centre and the greater rise in energy which the more diffuse *d* orbitals of this metal are likely to suffer on complex formation with the C_5H_5-ring ligands will cooperate to remove the lowest metal acceptor orbital far enough in energy from that of the acetyl oxygen lone pair to make a favourable η^2 geometry inaccessible.



This conclusion, that a limited energy separation between metal acceptor and ligand atom donor orbitals is critical for an η^2 geometry, is supported by observations on the cationic derivative $(C_5H_5)_2Nb(NCCH_3)^+$. The acetonitrile carbonyl cation $(C_5H_5)_2Nb(NCCH_3)(CO)^+$, available by ligand exchange from the THF adduct $(C_5H_5)_2Nb(THF)(CO)^+$ [9], loses its CO ligand upon irradiation. Concomitantly the stretching absorption of its R—C≡N ligand is shifted to 1640 cm^{-1}. The similarity of this R—C≡N frequency to that observed in the η^2-acetonitrile compound $(C_5H_5)_2Mo(NCCF)_3)$ [17] indicates that the ace-



tonitrile ligand in $(C_5H_5)_2Nb(NCCH_3)^+$ is similarly bicoordinated *. Apparently, the positive charge, which increases the acceptor strength of the metal centre, and the increased donor capability of the nitrogen over that of an oxygen ligand atom, cooperate in this acetonitrile derivative $(C_5H_5)_2Nb(NCCH_3)^+$ to make an η^2 geometry more favourable than in the reaction intermediate $(C_5H_5)_2Nb(OCCH_3)$. This observation would suggest that an η^2 acetyl intermediate, which would favour a ligand migration reaction by intermolecular electrophilic assistance, might be more easily accessible from a cationic species such as $(C_5H_5)_2Mo(CO)(CH_3)^+$ or $(C_5H_5)_2Mo(CO)H^+$ [12] and that the reactions of species of this kind should be included in a search for systems which might sustain catalytic reaction cycles for reduction of CO.

Experimental

All the complexes were handled under nitrogen in Schlenk vessels or on a vacuum manifold. For photoreactions a semi-circular quartz cell with two inlet fittings was used, and was placed close to a 125 Watt medium pressure mercury immersion lamp in an isopropanol/CO_2 cooling bath. Gases evolved were measured by a Toepler pump and identified by their IR spectra. Microanalyses were carried out by the Analytische Laboratorien, vorm. A. Bernhardt, Gummersbach, BRD.

Preparation of $(C_5H_5)_2Nb(CH_3)(CO)$ from $(C_5H_5)_2Nb(CH_3)Cl$.

When a solution of 137 mg (0.54 mmol) of $(C_5H_5)_2Nb(CH_3)_2$ [21] in diethyl ether was treated with 0.72 ml of a 0.75 *M* ethereal solution of HCl gas, the initially dark red solution turned brown. The residue after removal of HCl gas and solvent was extracted with petroleum ether to remove any remaining dimethyl compound. The residue was then dissolved in 80 ml of toluene. Addition of 80 ml of petroleum ether gave 90 mg of $(C_5H_5)_2Nb(CH_3)Cl$ (yield: 60% based on $(C_5H_5)_2Nb(CH_3)_2$) as a brown, crystalline precipitate. Elemental analysis: Found: C, 48.03, H, 4.68; Cl 12.82; Nb 33.92. $C_{11}H_{13}ClNb$ calcd.: C, 48.30; H, 4.79; Cl 12.96; Nb 33.97%.

To a solution of 233 mg (0.85 mmol) of $(C_5H_5)_2Nb(CH_3)Cl$ in 60 ml of toluene, 0.6 ml of sodium amalgam containing 2.1 mmol Na/ml are added in a 200 ml flask. The vessel is filled with an atmosphere of CO, closed and cautiously shaken. After several minutes, the initially brown solution turns blue; after 2—3 h a green solution of $(C_5H_5)_2Nb(CH_3)(CO)$ is obtained. After careful removal of amalgam by filtration and evaporation of the solvent, the product is

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* Alternatively, this species could arise from a coupling reaction similar to that observed for some niobium(III), tantalium(III) and titanium(III) acetonitrile complexes [18,19]. However, these coupling products have IR absorptions different from those observed for $(C_5H_5)_2Nb(NCCH_3)^+$ and $(C_5H_5)_2Mo(NCCF_3)$.

TABLE 1

^{1}H NMR DATA FOR METHYLNIOBOCENE-LIGAND DERIVATIVES $(C_5H_5)_2Nb(CH_3)L$ ALL SPECTRA TAKEN IN TOLUENE-d_8 AT 100 MHz.

L =	$P(OCH_3)_3$	$P(C_2H_5)_3$	C_2H_4
Chemical shifts (ppm relative to τ_{TMS} = 10.0)			
$(C_5\underline{H}_5)_2$	5.40	5.58	5.98
$M-C\underline{H}_3$	10.31	10.58	10.40
$C\underline{H}_2$	—	8.74	9.14 — 9.32 (A_2B_2)
$O-C\underline{H}_3$, $C-C\underline{H}_3$	6.72	9.19	—
Coupling constants (Hz)			
$\underline{P}-M-C_5\underline{H}_5$	3	2	—
$\underline{P}-M-C\underline{H}_3$	7	7	—
$\underline{P}-O-C\underline{H}_3$	10	—	—

sublimed in vacuo at 50—60°C (yield: 50—60%, based on $(C_5H_5)_2Nb(CH_3)Cl$). Elemental analysis: Found: C, 53.85; H, 5.06; Nb, 35.15. $C_{12}H_{13}NbO$ calcd.: C, 54.15; H, 4.92; Nb 34.91%. ^{1}H NMR: Singlets at 5.46 (10) and 10.35 (3) ppm.

The methyl carbonyl derivative $(C_5H_5)_2Nb(CH_3)(CO)$ is air-sensitive. If its solutions are exposed to air it is quantitatively converted into the methyl oxo derivative, $(C_5H_5)_2Nb(CH_3)O$, which is characterized by a ^{1}H NMR spectrum with singlets at 4.42 (10) and 8.92 (3) ppm and by a mass spectrum with parent ion at *m/e* 254 and fragment ions at *m/e* 239 $(C_5H_5)_2NbO^+$) and 238 ($(C_5H_5)_2NbCH_3^+$).

Syntheses of other methyl ligand derivatives $(C_5H_5)_2Nb(CH_3)L$ with L = $P(OCH_3)_3$, $P(C_2H_5)_3$ or C_2H_4 were carried out analogously. These substances were purified by extraction with petroleum ether and characterized by mass spectra which showed the appropriate parent ions and fragment ions $(C_5H_5)_2NbCH_3^+$ and $(C_5H_5)_2NbL^+$ and by the NMR data listed in Table 1.

Acknowledgements

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