Synthesis, Electrochemistry and Reactivity of Formato- and Acetato-Niobocene Complexes†

Antonio Antiñolo,[a] **Mariano Fajardo,**[b] **Santiago García-Yuste,**[a] **Isabel del Hierro,**[a] **Antonio Otero,***[,a] **Soumia Elkrami,**[c] **Youssef Mourad**[c] **and Yves Mugnier**[c]

[a] *Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas, Campus Universitario, Universidad de Castilla la Mancha, 13071-Ciudad Real, Spain*

[b] *Departamento de Química Inorgánica, Campus Universitario, Universidad de Alcalá, 28871-Alcalá de Henares, Spain*

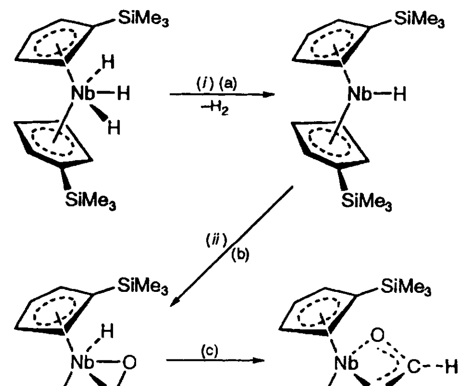
[c] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, CNRS URA 1685, Faculté des Sciences Gabriel, 6, bd Gabriel 21000 Dijon, France*

The complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3]$ **1** reacted with CO_2 to give the formato complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}]$ **2**, which can alternatively be prepared from a two-electron reduction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ **3** in the presence of formic acid. The reaction of **2** with different π-acids or heterocumulene molecules resulted in opening of the bidentate formate ligand giving rise to the monodentate formato-containing complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O\}L]$, L = CS_2 **4**, CO **5** or 2,6-$Me_2C_6H_3NC$ **6**. On the other hand, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O,O'\}]$ **8** was prepared from either the reaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ **7** with 1 equivalent of $Tl(O_2CMe)$ or from a two-electron reduction of **3** in the presence of acetic acid. The complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(MeCOCHCOMe\text{-}O,O')]$ **9** can also be isolated from the reaction of **7** with 1 equivalent of Tl(acac) (acac = acetylacetonate). Complex **8** reacted with oxygen to give $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2O\{OC(O)Me\text{-}O\}]$ **10**, and with π-acids or heterocumulenes to give products with a monodentate OC(O)Me ligand, namely $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O\}L]$, L = CS_2 **11**, SCNPh **12**, PhNCCPhEt **13**, $MeO_2CC{\equiv}CCO_2Me$ **14**, Bu^tNC **15** or CO **16**. The structures of all complexes have been established by spectroscopic methods.

Metal-promoted transformations of carbon dioxide constitute an attractive goal which have stimulated widespread interest. While a number of discrete CO_2-containing metal complexes have been described,[1] few reactivity studies of co-ordinated CO_2 are known. Insertions of unsaturated molecules into metal–hydride or carbon bonds are considered as fundamental chemical steps in several catalytic cycles and frequently lead to reactive intermediates. Hence metalloformates M–OC(O)H derived from carbon dioxide insertion into M–H bonds are known to be involved in the catalytic hydrogenation of these compounds to formic acid and its derivatives.[2] Similarly, the insertion of carbon dioxide into M–C bonds produces O-bound carboxylato complexes.[3] Recently, in connection with our studies of metal-promoted activations of heterocumulenes such as ketene and ketenimine with niobocene complexes,[4] the formation of carbon dioxide–niobocene compounds was discovered.[5] Continuing our studies, in this article we report our results on the reactivity of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3]$ **1** toward CO_2. This has allowed us to isolate a formato derivative, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}]$ **2**, which can also be formed from the electroreduction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ **3** in the presence of formic acid. In addition we report the chemical and electrochemical preparations of an acetato complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O,O'\}]$, as well as several aspects related to its reactivity.

Results and Discussion

First, the interaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3]$ **1** with carbon dioxide was investigated. The standard reaction procedure involved heating a stirred saturated CO_2 solution of **1** at 60 °C for 6 h, which permitted the isolation of the formato complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}]$ **2** as a brown, air-sensitive oily product after appropriate work-up [equation (1)].



Scheme 1 (*i*) Heat; (*ii*) CO_2

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3] + CO_2 \longrightarrow [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}] + H_2 \quad (1)$$

The isolation of complex **2** as the product from this reaction can be understood in terms of Scheme 1. Step (a) corresponds to

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† *Non-SI unit employed:* atm = 101 325 Pa.

the elimination of H_2 and the formation of a very reactive sixteen-electron monohydride niobocene species, which has previously been proposed in several processes.[6] Co-ordination of CO_2 to this unsaturated species to give an eighteen-electron hydride–carbon dioxide intermediate is suggested in step (b), though no experimental data exist to confirm this suggestion since all attempts to detect it, including several ^1H and ^{13}C NMR experiments, were unsuccessful, probably because under the required experimental conditions, *i.e.* heating at 60 °C, the subsequent step would be too fast and thus prevent detection. The final step (c) corresponds to the insertion of the co-ordinated CO_2 into the Nb–H bond to give the formate ligand.[7] Nicholas and co-workers[8] have recently published data which confirm the formation of a hydride–carbon dioxide tantalocene intermediate at -40 °C as well as the subsequent insertion to give formato–niobocene and –tantalocene derivatives. It is noteworthy that preco-ordination of CO_2 followed by a subsequent insertion process into an M–H bond were discounted in several cases,[9] and as far as we are aware the proposed mechanism was confirmed for the first time in the above-mentioned tantalocene example. Therefore the formation of complex **2** *via* the steps outlined in Scheme 1 is proposed with caution, since an alternative pathway which implies direct insertion of CO_2 into the Nb–H bond without co-ordination cannot be excluded.

Reactivity studies on complex **2** have been carried out. Reaction with CS_2 or the π-acids CO and $2,6\text{-}Me_2C_6H_3NC$ gives rise to the transformation from a bidentate to monodentate formate as a consequence of co-ordination of the incoming ligand, in accordance with equation (2), L = CS_2 **4**,

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}] + L \longrightarrow [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O\}L] \quad (2)$$

CO **5** or $2,6\text{-}Me_2C_6H_3NC$ **6**. Complexes **4** and **6** were isolated, after appropriate work-up, as air-sensitive solids in good yields. However with other L, such as phosphites $P(OR)_3$, the transformation has never been observed; this behaviour suggests that the presence of a heterocumulene like CS_2 which is able to co-ordinate strongly to the niobium atom as a bidentate ligand[10] or strong π acceptors are necessary to break an Nb–O bond and to transform bidentate into monodentate formate. Alternatively, complex **5** can be prepared from the reaction of the hydrido complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(CO)]$ with CO_2, through an insertion into the Nb–H bond.

Infrared and especially NMR spectroscopy have proved to be useful for characterization of the formato and other complexes (see below). In the carboxylate (including formate) complexes, the CO_2^- stretching frequencies are usually the most prominent feature of their IR spectra and attention was focused upon those. The usual approach has been to relate the values of Δ [the separation between $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$] with the mono- or bi-dentate character of the ligands.[11] The IR spectrum of **2** shows two bands at 1638 and 1545 cm^{-1} which correspond to $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ respectively; the value $\Delta = 93\ cm^{-1}$ is significantly less than the 'ionic' value, $\Delta = 201\ cm^{-1}$,[12] which indicates that the formate ligand in **2** acts as a bidentate group. Moreover, the ^1H and ^{13}C NMR data confirm the bidentate co-ordination. In fact, the observation of two and three signals for each cyclopentadienyl ring in the ^1H and ^{13}C NMR spectra respectively indicates the presence of a symmetrical environment, **a**. In addition, the presence of a formate ligand was demonstrated by the resonances at δ 7.47 (O_2CH) and 184.3 (O_2CH) in the ^1H and ^{13}C NMR spectra respectively [confirmed by a distortionless enhancement of polarization transfer (DEPT) experiment]. In the light of these data an alternative structure for **2** as 1-metallated formic acid **b** can be excluded.

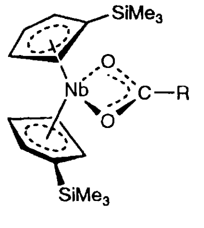
The IR spectra of complexes **4**–**6** showed the $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ to have Δ values of 332, 318 and 318 cm^{-1} respectively, which are consistent with the presence of a monodentate formate ligand.[11] Again the NMR data confirm this; the ^1H and ^{13}C spectra show four and five signals respectively for each cyclopentadienyl ring in accordance with a lack of symmetry in structure **c**. Carbon and proton resonances for the formate ligands appear at δ 168.8, 169.7, 170.4 (O_2CH) and 8.77, 8.41, 8.59 (O_2CH, confirmed by DEPT experiments) for **4**, **5** and **6** respectively. In addition, ^{13}C NMR spectra show additional characteristic signals for the ancillary ligands, namely at δ 305.5 (CS_2), 254.5 (CO) and 208.0 ($CNC_6H_3Me_2$) for complexes **4**, **5** and **6**.

We have also carried out the preparation of acetato–niobocene complexes. The reaction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ **7** with 1 equivalent of $Tl(O_2CMe_3)$ gives, after appropriate work-up, the acetato complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O,O'\}]$ **8** [equation (3)]. Previously[13] some carboxylate–niobocene complexes have been described and characterized.

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl] + Tl(O_2CMe) \longrightarrow [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O,O'\}] + TlCl \quad (3)$$

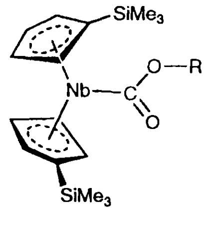
The acetylacetonato complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(MeCOCHCOMe\text{-}O,O')]$ **9** was similarly prepared from the reaction of **7** with 1 equivalent of Tl(acac) (acac = acetylacetonate). Complexes **8** and **9** were isolated as air-sensitive materials. Hexane solutions of **8** were easily oxidized by exposure to air to give the oxo-complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2O\{OC(O)Me\text{-}O\}]$ **10** in quantitative yield.

The IR spectrum of complex **8** shows $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ at 1631 and 1528 cm^{-1} respectively, with $\Delta = 103\ cm^{-1}$ significantly less than the 'ionic' value of $\Delta = 164\ cm^{-1}$,[11] indicating that the acetate ligand acts as bidentate group. Proton and ^{13}C NMR spectra support this proposal (see Experimental section), confirming that a symmetrical structure



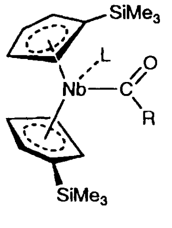
a

2 R = H
8 R = Me



b

R = H or Me



c

R = H, L = CS_2 **4**, CO **5** or $2,6\text{-}Me_2C_6H_3NC$ **6**
R = Me, L = O **10**, CS_2 **11**, SCNPh **12**,
PhNCCPhEt **13**, $MeO_2CC{\equiv}CCO_2Me$ **14**,
Bu^{t}NC **15**, CO **16**, or PhNCCHPhEt **17**

must be considered (see **a**); the ^{13}C resonance for the acetate ligand appears at δ 196. Again an alternative structure for **8** as a 1-metallated formato ether (**b**) can be excluded. For complex **9** two IR bands appear at 1590 and 1524 cm^{-1} which correspond to ν(C⋯C) coupled with ν(C⋯O), and ν(C⋯O) coupled with ν(C⋯C) respectively.[14] In addition, the ^1H and ^{13}C NMR data again (see Experimental section) confirm that a symmetrical structure is present; ^{13}C resonances for the CH and CO carbons of acac appear at δ 101.7 and 190.9 respectively.

Finally, in a study parallel to that carried out on complex **2** (see above), the reactivity of **8** towards several heterocumulene and π-acids was tested. It reacts with 1 equivalent of L = [CS_2 **11**, SCNPh **12**, PhNCCPhEt **13**, $MeO_2CC{\equiv}CCO_2Me$ **14**, Bu^{t}NC **15** or CO **16**] to give a family of monodentate acetato–niobocene complexes, [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O\}L$]. The formation of these complexes as well as that of **10** can again be explained as resulting from an opening of the OC(O)Me-*O,O′* group in **8** by co-ordination of the new ligands, leaving an OC(O)Me-*O* ligand.

Protonation of complex **13** with $HBF_4{\cdot}OEt_2$ affords an iminoacyl derivative [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O\}(\eta^2\text{-}PhNCCHPhEt)]^+BF_4^-$ **17**, similar to those found previously[4c] for several ketenimine niobocene derivatives.

Based on $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$ in complexes **10**–**17** the acetate acts as a monodentate ligand. The values for Δ (see Experimental section) are much greater than the 'ionic' value (see below).[11] The IR spectrum of **12** shows a band at 1573 cm^{-1} for ν(C=N), which is consistent with a η^2-(C,S) rather than a η^2-(C,N) co-ordination mode for the isothiocyanate ligand. The ν(N=C=C) band for the ketenimine ligand in **13** appears at 1588 cm^{-1} which is in accordance with data previously reported for other ketenimine complexes where a η^2-(C,N) co-ordination mode was found.[4a] Finally, the IR ν(C=N) iminoacyl absorption for **17** appears at 1580 cm^{-1} in accord with previously reported values for structurally characterized η^2-iminoacyl complexes.[4c] Similar to complexes **4**–**6**, the ^1H and ^{13}C NMR data (see Experimental section) for **10**–**17** agree with a lack of symmetry in their structures (**c**). For complex **13** two isomers *E* and *Z* are obtained in a ratio 80:20 similar to other analogous ketenimine–halogeno complexes. The ^{13}C resonances for the acetate carbon atom appear at *ca.* δ 178. Other additional ^{13}C resonances to be considered for the ancillary ligands are, δ 309.0 (CS_2) in **11**, 215.5 (S*C*NPh) **12**, 150.0 (PhN=*C*=CPhEt) **13**, 171.5 and 141.9 ($MeO_2C\mathit{C}{\equiv}\mathit{C}CO_2Me$) **14**, 213.9 (Bu^{t}N*C*) **15**, 254.1 (CO) **16** and 221.0 (PhN*C*CHPhEt) **17** (see Experimental section).

Electrochemical Studies.—Electrochemical studies on [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$] **3** in the presence of both formic and acetic acids in thf–$NaBPh_4$ solution were carried out. The polarogram of **3** in the presence of 2 equivalents of HCO_2H shows only a reduction wave A [Fig. 1(*a*)], the height of which is twice that obtained in the absence of formic acid; in cyclic voltammetry on a vitreous carbon electrode the corresponding reduction peak A (E_p = −0.98 V at 0.2 V s^{-1}) is also observed. Reversal of the scan potential produces an oxidation peak F_1' (E_p = −0.26 V at 0.2 V s^{-1}). In the second scan a new reduction peak F_1 (E_p = −0.42 V at 0.2 V s^{-1}) located at a lower cathodic potential than that of A is present [Fig. 2(*a*) and (*b*)]. When an electrolysis of **3** is performed at room temperature in the presence of formic acid at the potential of wave A, two electrons per molecule of **3** are consumed and the polarogram of the resulting solution exhibits wave F_1' [Fig. 1(*b*)]. Cyclic voltammetry inversion of the scan potential after peak F_1' causes two reduction peaks F_1 and F_2* to appear [Fig. 2(*c*)].

These results can be rationalized if we assume that the two-electron reduction of complex **3** gives **2**, in accordance with the following overall reaction (4). It has been established that the

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2] + HCO_2H + 2e^- \longrightarrow [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}] + 2Cl^- + \tfrac{1}{2}H_2 \quad (4)$$

well defined reversible system F_1'–F_1 (see Fig. 1) corresponds to **2**, because when the reaction of **1** with CO_2 was carried out in a thf–NBu_4PF_6 solution to give **2**, the cyclic voltammogram showed the reversible system F_1'–F_1.

We propose that **2** undergoes, within the cyclic voltammetry time-scale, a reversible one-electron oxidation to give, presumably, a cationic species [equation (5)]. This cationic

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}] \underset{F_1}{\overset{F_1'}{\rightleftharpoons}} [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}]^+ \quad (5)$$

species, which is relatively stable in THF–$NaBPh_4$ solution within the cyclic voltammetry time span, is reduced at the potential of peak F_1. On the other hand, cationic species such as [$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O\}(thf)]^+$ are proposed to be responsible for the reduction peak F_2* [see Fig. 2(*c*)], but no spectroscopic data can be supplied because of their instability during the electrolysis time span.

The two-electron reduction of complex **3** in thf–$NaBPh_4$ solution in the presence of 2 equivalents of acetic acid gave **8**, in accordance with the following overall reaction (6). A well

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2] + HO_2CMe + 2e^- \longrightarrow [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O,O'\}] + 2Cl^- + \tfrac{1}{2}H_2 \quad (6)$$

defined reversible system F_2'–F_2 (F_2', E_p = −0.44 V at 0.2 V s^{-1}; F_2, E_p = −0.54 V at 0.2 V s^{-1}) which corresponds to **8** was observed, in accordance with the reversible one-electron oxidation (7). Furthermore, we have confirmed that the cyclic

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O,O'\}] \underset{F_2}{\overset{F_2'}{\rightleftharpoons}} [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O,O'\}]^+ \quad (7)$$

voltammogram of an isolated sample of **8** shows the reversible system F_2'–F_2.

Conclusion

The chemical and electrochemical synthesis of bidentate formato– and acetato–niobocene complexes, and the chemical preparation of the first involved insertion of CO_2 into an Nb–H bond have been reported. In addition, the reactivity of both complexes towards several heterocumulene and π-acids was studied, from which a facile bidentate ⟶ monodentate

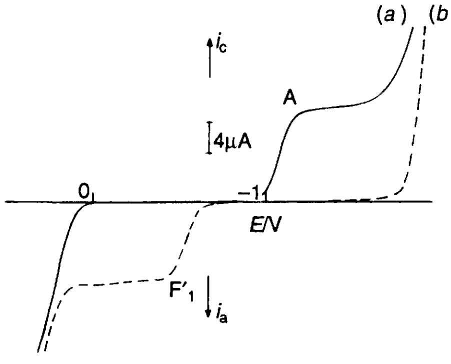


Fig. 1 Polarograms (average current) of complex **3** in thf–$NaBPh_4$ (0.2 mol dm^{-3}) in the presence of 2 equivalents of formic acid: (*a*) before electrolysis; (*b*) after two-electron reduction at −1.4 V

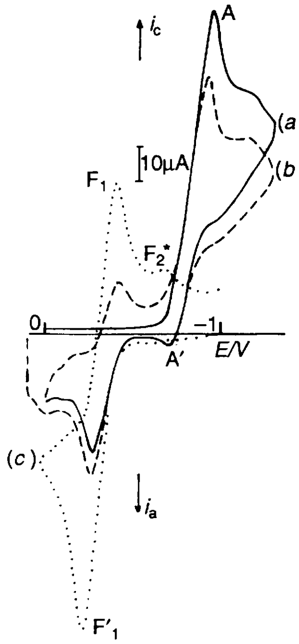


Fig. 2 Cyclic voltammograms of complex **3** in thf–$NaBPh_4$ (0.2 mol dm^{-3}) in the presence of 2 equivalents of formic acid. Sweep rate 0.2 V s^{-1}. Starting potential: (*a*) and (*b*) 0 V; (*c*) −1 V. (*a*) First scan; (*b*) second scan; (*c*) after two-electron reduction. The potential of the ferrocene–ferrocenium couple under our experimental conditions was 0.535 V

conversion of the co-ordination mode of the carboxylate ligand was observed by IR, ^1H and ^{13}C NMR spectra.

Experimental

General Procedures.—All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyser. Infrared spectra were obtained in the region 4000–200 cm^{-1} using a Perkin-Elmer 883 spectrophotometer, ^1H and ^{13}C NMR spectra on Varian Unity FT-300 and Gemini FT-200 spectrometers and referenced to the residual deuteriated solvent. Cyclic voltammetry experiments were carried out in a standard three-electrode Tacussel UAP4 unit cell. The reference was a saturated calomel electrode (SCE), separated from the solution by a sintered-glass disc. The auxiliary electrode was a platinum wire. For all voltammetric measurements, the working electrode was vitreous carbon and for the polarograms a three-electrode Tacussel Tipol polarograph was used. The dropping-mercury electrode characteristics were $m = 3$ mg s^{-1} and $\tau = 0.5$ s. For controlled-potential electrolysis, a mercury pool was used as the cathode and a platinum plate as an anode, the latter being separated from the solution by a sintered-glass disc. Large-scale electrolyses were carried out in a cell with three compartments separated with fritted glass of medium porosity. In all cases the electrolyte was a 0.2 mol dm^{-3} solution of $NaBPh_4$ in thf. The electrolyses were performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator. The salt $NaBPh_4$ was obtained from Fluka (puriss.p.a. for electrochemical grade) and dried and deoxygenated before use. The complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ **3**, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ **7** and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3]$ **1** were prepared as reported previously.[15–17]

Preparations.—$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}]$ **2**. A thf (40 cm^3) solution of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3]$ (0.30 g, 0.81 mmol) was saturated with CO_2 and stirred for 6 h at 60 °C. The solution became increasingly red and a brown solution was finally obtained which was evaporated to dryness and the residue extracted with hexane. Complex **2** was obtained as a brown oily material after evaporation of the solvent. Yield 0.32 g, 95%. IR(Nujol): $\nu_{asym}(CO_2^-)$ 1638, $\nu_{sym}(CO_2^-)$ 1545 cm^{-1}. NMR (C_6D_6): ^1H, δ −0.04 (s, 18 H, $SiMe_3$), 4.14 (4 H), 5.68 (4 H, m, $C_5H_4SiMe_3$) and 7.47 (s, 1 H, O_2CH); $^{13}C\text{-}\{^1H\}$, δ 0.05 ($SiMe_3$), 107.8 (C_{ipso}), 105.0, 108.1 ($C_5H_4SiMe_3$) and 184.3 (O_2CH).

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O\}L]$ (L = CS_2 **4**, CO **5** *or* 2,6-$Me_2C_6H_3NC$ **6**). To a solution in hexane (30 cm^3) of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)H\text{-}O,O'\}]$ **2** (0.25 g, 0.60 mmol) was added an equimolar quantity of CS_2. The mixture was stirred for 0.5 h at room temperature after which an orange microcrystalline precipitate of complex **4** was obtained. It was filtered off, washed with cold hexane and dried under vacuum, yield 0.23 g (80%). Complexes **5** and **6** were prepared in a similar way. After stirring the corresponding mixtures, a thf solution of **2** saturated with CO at 3 atm in a Fisher–Porter bottle during 2 d and thf solution of **2** with an equimolar quantity of 2,6-$Me_2C_6H_3NC$ during 0.5 h respectively, brown solutions were formed which were evaporated to dryness. The residues were washed with cold hexane and complexes **5** and **6** were isolated as red solids, yields 0.24 (90) and 0.25 g (90%) (Found: C, 44.15; H, 5.15. Calc. for $C_{18}H_{27}NbO_2S_2Si_2$ **4**: C, 44.25; H, 5.55. Found: C, 49.20; H, 6.25. Calc. for $C_{18}H_{27}NbO_3Si_2$ **5**: C, 49.10; H, 6.15. Found: C, 59.50; H, 6.60; N, 2.60. Calc. for $C_{26}H_{36}NbNO_2Si_2$ **6**: C, 57.45; H, 6.65; N, 2.60%).

Complex **4**: IR (Nujol) $\nu_{asym}(CO_2^-)$ 1617, $\nu_{sym}(CO_2^-)$ 1285, $\nu(C{=}S)$ 1146 cm^{-1}; ^1H NMR (C_6D_6) δ 0.05 (s, 18 H, $SiMe_3$), 4.97 (2 H), 5.45 (2 H), 6.00 (2 H), 6.18 (2 H) (m, $C_5H_4SiMe_3$) and 8.77 (s, 1 H, O_2CH); $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6) δ −1.02 ($SiMe_3$), 107.3, 107.5, 122.0, 122.8 (C_{ipso}), 127.5 ($C_5H_4SiMe_3$), 168.8 (O_2CH) and 305.5 (CS_2).

Complex **5**: IR (Nujol) $\nu_{asym}(CO_2^-)$ 1618, $\nu_{sym}(CO_2^-)$ 1300, $\nu(CO)$ 1917 cm^{-1}; ^1H NMR (C_6D_6) δ 0.05 (s, 18 H, $SiMe_3$), 4.73 (2 H), 4.99 (2 H), 5.10 (4 H, m, $C_5H_4SiMe_3$) and 8.41 (s, 1 H, O_2CH); $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6) δ −0.12 ($SiMe_3$), 95.0, 98.7 (C_{ipso}), 103.7, 104.6 ($C_5H_4SiMe_3$), 169.7 (O_2CH) and 254.5 (CO).

Complex **6**: IR (Nujol) $\nu_{asym}(CO_2^-)$ 1619, $\nu_{sym}(CO_2^-)$ 1301, $\nu(C{=}N)$ 1746 cm^{-1}; ^1H NMR (C_6D_6) δ 0.05 (s, 18 H, $SiMe_3$), 2.31 (s, 6 H, 2,6-$Me_2C_6H_3NC$), 4.18 (2 H), 5.20 (2 H), 5.64 (4 H, m, $C_5H_4SiMe_3$), 6.68 (m, 3 H, 2,6-$Me_2C_6H_3NC$) and 8.59 (s, 1 H, O_2CH); $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6) δ 0.14 ($SiMe_3$), 19.1 (2,6-$Me_2C_6H_3NC$), 95.9, 97.2 (C_{ipso}), 100.1, 103.1, 108.4 ($C_5H_4SiMe_3$), 126.4, 127.8, 129.4, 132.7 (2,6-$Me_2C_6H_3NC$), 170.4 (O_2CH) and 208 (2,6-$Me_2C_6H_3NC$).

$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{OC(O)Me\text{-}O,O'\}]$ **8** *and* $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(MeCOCHCOMe\text{-}O,O')]$ **9**. To a solution in hexane (40 cm^3) of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]$ **7** (0.73 g, 1.82 mmol) was added powdered $Tl(O_2CMe)$ (0.48 g, 1.82 mmol) and stirred for 2 h. The initial purple solution became increasingly green-brown and a green suspension was finally obtained. The suspension was filtered through a layer of Celite and the filtrate evaporated to dryness to give a green solid, which was washed with cold hexane and dried under vacuum (Found: C, 50.30; H, 6.80. Calc. for $C_{18}H_{29}NbO_2Si_2$ **8**: C, 50.70; H, 6.55%). Yield 0.70 g (90%). Complex **9** was prepared in a similar way and was isolated as an oily green product. Yield 0.76 g (90%).

Complex **8**: IR (Nujol) $\nu_{asym}(CO_2^-)$ 1631, $\nu_{sym}(CO_2^-)$ 1528 cm^{-1}; ^1H NMR (C_6D_6) δ 0.06 (s, 18 H, $SiMe_3$), 0.22 (s, 3 H, O_2CCH_3), 4.20 (4 H), 5.74 (4 H, m, $C_5H_4SiMe_3$); $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6) δ 0.49 ($SiMe_3$), 23.7 (O_2CCH_3), 96.1 (C_{ipso}), 104.7, 107.4 ($C_5H_4SiMe_3$) and 196 (O_2CCH_3).

Complex **9** IR (Nujol) $\nu(C{\cdots}C)$ coupled with $\nu(C{\cdots}O)$ 1590, $\nu(C{\cdots}O)$ coupled with $\nu(C{\cdots}C)$ 1524 cm^{-1}; ^1H NMR (C_6D_6) δ 0.13 (s, 18 H, $SiMe_3$), 1.36 (s, 6 H, $CH_3COCHCOCH_3$), 4.91 (s, 1 H, $CH_3COCHCOCH_3$), 4.47 (4 H), 5.63 (4 H, m, $C_5H_4SiMe_3$); $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6) δ 0.59 ($SiMe_3$), 26.9

$(C\mathrm{H_3COCHCO}C\mathrm{H_3})$, 101.7 $(\mathrm{CH_3CO}C\mathrm{HCOCH_3})$, 104.6 (C_{ipso}), 104.9, 109.1 $(C_5\mathrm{H_4SiMe_3})$ and 190.9 $(\mathrm{CH_3}C\mathrm{OCH}C\mathrm{OCH_3})$.

$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\{\mathrm{OC(O)Me}\text{-}O\}\mathrm{L}]$ (L = O **10**, $\mathrm{CS_2}$ **11**, SCNPh **12**, PhNCCPhEt **13**, $\mathrm{MeO_2CC{\equiv}CCO_2Me}$ **14**, $\mathrm{Bu^tNC}$ **15**, CO **16** *or* PhNCCHPhEt **17**). Carbon disulfide (0.50 mmol) was added to a solution in hexane (30 $\mathrm{cm^3}$) of $[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_4H_4SiMe_3})_2\{\mathrm{OC(O)Me}\text{-}O,O'\}]$ **8** (0.20 g, 0.47 mmol). The mixture was stirred for 3 h at room temperature and an orange precipitate was formed. The suspension was filtered and the resulting solution concentrated giving rise again to a new fraction of the orange product, which was filtered. Both samples of the orange solid, which corresponds to complex **11**, were washed with cold hexane and dried under vacuum, yield 0.22 g (93%). Complex **14** was obtained similarly as a brown-orange solid (0.25 g, 92%). In the preparations of **12**, **13** and **15**, after stirring the reaction mixtures, in hexane as solvent, for 12, 16 and 3 h respectively, solutions were formed which were evaporated to dryness. The residues were washed with cold hexane and the complexes isolated as brown-green **12** (0.25, 95), yellow **13** (0.29, 97) and red **15** (0.21 g, 90%) oily products.

Complex **16** was obtained as brown microcrystals in a similar way to that of **12**, **13** and **15** when a thf solution of **8** saturated with CO (3 atm in a Fisher–Porter bottle) was stirred over 4 h. Yield 0.19 g (92%).

Through a solution in hexane (30 $\mathrm{cm^3}$) of complex **8** (0.20 g, 0.47 mmol) was bubbled $\mathrm{O_2}$, and after stirring for 2 h a yellow solution was finally obtained, which was evaporated to dryness to give complex **10** as a yellow solid (0.18 g, 85%).

To an $\mathrm{Et_2O}$ (30 $\mathrm{cm^3}$) solution of complex **13** (0.34 g, 0.53 mmol) at −78 °C was added $\mathrm{HBF_4{\cdot}Et_2O}$ (0.53 mmol). The mixture was stirred and allowed to warm to room temperature for 0.5 h. The resulting suspension was filtered and the yellow solid, which corresponds to complex **17**, was washed with cold $\mathrm{Et_2O}$ and dried under vacuum. Yield 0.26 g (87%) (Found: C, 48.75; H, 6.35. Calc. for $\mathrm{C_{18}H_{29}NbO_3Si_2}$ **10**: C, 48.85; H, 6.50. Found: C, 45.70; H, 5.65. Calc. for $\mathrm{C_{19}H_{29}NbO_2S_2Si_2}$ **11**: C, 45.40; H, 5.75. Found: C, 50.35; H, 5.95. Calc. for $\mathrm{C_{24}H_{35}NbO_6Si_2}$ **14**: C, 50.70; H, 6.20. Found: C, 50.35; H, 6.35. Calc. for $\mathrm{C_{19}H_{29}NbO_3Si_2}$ **16**: C, 50.20; H, 6.45. Found: C, 55.20; H, 5.90; N, 1.70. Calc. for $\mathrm{C_{34}H_{44}BF_4NNbO_2Si_2}$ **17**: C, 55.50; H, 6.15; N, 1.90%).

Complex **10**: IR (Nujol) $\nu_{\mathrm{asym}}(\mathrm{CO_2^-})$ 1714, $\nu_{\mathrm{sym}}(\mathrm{CO_2^-})$ 1437 $\mathrm{cm^{-1}}$; ^{1}H NMR $(\mathrm{C_6D_6})$ δ 0.21 (s, 18 H, $\mathrm{SiMe_3}$), 2.15 (s, 3 H, $\mathrm{O_2CCH_3}$), 5.43 (2 H), 5.90 (2 H), 5.95 (2 H) and 6.29 (2 H, m, $\mathrm{C_5}H_4\mathrm{SiMe_3}$); ^{13}C-{^{1}H} NMR $(\mathrm{C_6D_6})$ δ −1.21 $(\mathrm{SiMe_3})$; 25.0 $(\mathrm{O_2C}C\mathrm{H_3})$, 90.1 (C_{ipso}), 105.4, 112.2, 123.9, 125.1 $(C_5\mathrm{H_4SiMe_3})$ and 188.0 $(\mathrm{O_2}C\mathrm{CH_3})$.

Complex **11**: IR (Nujol) $\nu_{\mathrm{asym}}(\mathrm{CO_2^-})$ 1615, $\nu_{\mathrm{sym}}(\mathrm{CO_2^-})$ 1412 $\mathrm{cm^{-1}}$; ^{1}H NMR $(\mathrm{CDCl_3})$ δ 0.01 (s, 18 H, $\mathrm{SiMe_3}$), 1.95 (s, 3 H, $\mathrm{O_2CC}H_3$), 5.63 (2 H), 6.00 (4 H), 6.18 (2 H, m, $\mathrm{C_5}H_4\mathrm{SiMe_3}$); ^{13}C-{^{1}H} NMR $(\mathrm{CDCl_3})$ δ −1.14 $(\mathrm{SiMe_3})$, 27.0 $(\mathrm{O_2C}C\mathrm{H_3})$, 122.1 (C_{ipso}), 105.0, 106.0, 124.0, 126.0 $(C_5\mathrm{H_4SiMe_3})$, 178.0 $(\mathrm{O_2}C\mathrm{CH_3})$ and 309.0 $(\mathrm{CS_2})$.

Complex **12**: IR (Nujol) $\nu_{\mathrm{asym}}(\mathrm{CO_2^-})$ 1610, $\nu_{\mathrm{sym}}(\mathrm{CO_2^-})$ 1438, ν(C=N) 1573 $\mathrm{cm^{-1}}$; ^{1}H NMR $(\mathrm{C_6D_6})$ δ 0.06 (s, 18 H, $\mathrm{SiMe_3}$), 2.15 (s, 3 H, $\mathrm{O_2CCH_3}$), 4.97 (2 H), 5.58 (2 H), 6.22 (2 H, m, $\mathrm{C_5}H_4\mathrm{SiMe_3}$) and 7.00–7.70 (m, 5 H, SCNPh); ^{13}C-{^{1}H} NMR $(\mathrm{C_6D_6})$ δ −0.77 $(\mathrm{SiMe_3})$, 25.9 $(\mathrm{O_2C}C\mathrm{H_3})$, 120.6 (C_{ipso}) 103.2, 106.1, 121.6, 125.3 $(C_5\mathrm{H_4SiMe_3})$, 122.1, 124.9, 129.8 $(\mathrm{SCN}Ph)$, 177.9 $(\mathrm{O_2}C\mathrm{CH_3})$ and 215.5 $(\mathrm{S}C\mathrm{NPh})$.

Complex (*E*)-**13**: IR (Nujol) $\nu_{\mathrm{asym}}(\mathrm{CO_2^-})$ 1634, $\nu_{\mathrm{sym}}(\mathrm{CO_2^-})$ 1483, ν(N=C=C) 1588 $\mathrm{cm^{-1}}$; ^{1}H NMR $(\mathrm{CDCl_3})$ δ 0.16 (s, 18 H, $\mathrm{SiMe_3}$), 2.20 (s, 3 H, $\mathrm{O_2CCH_3}$), 2.60 (q, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 3.50 (t, 3 H, $\mathrm{CH_2C}H_3$), 4.94 (2 H), 5.92 (2 H), 5.97 (2 H), 6.28 (2 H, m, $\mathrm{C_5}H_4\mathrm{SiMe_3}$) and 6.70–7.40 (m, 5 H, Ph); ^{13}C-{^{1}H} NMR $(\mathrm{C_6D_6})$ δ −0.77 $(\mathrm{SiMe_3})$, 25.9 $(\mathrm{O_2C}C\mathrm{H_3})$, 120.6 (C_{ipso}), 103.2, 106.1, 121.6, 125.3 $(C_5\mathrm{H_4SiMe_3})$, 140.56, 146.80 ($\mathrm{C^1}$ of Ph), 121.54, 123.50, 123.62, 127.32, 127.83 (Ph).

Complex **14**: IR (Nujol) $\nu_{\mathrm{asym}}(\mathrm{CO_2^-})$ 1622, $\nu_{\mathrm{sym}}(\mathrm{CO_2^-})$ 1432, ν(C≡C) 1733 $\mathrm{cm^{-1}}$; ^{1}H NMR $(\mathrm{CDCl_3})$ δ 0.22 (s, 18 H, $\mathrm{SiMe_3}$), 1.99 (s, 3 H, $\mathrm{O_2CCH_3}$), 3.85, 3.76 (s, 3 H, $\mathrm{MeO_2CC{\equiv}CCO_2Me}$), 5.93 (2 H), 6.06 (2 H), 6.19 (2 H), 6.30 (2 H, m, $\mathrm{C_5}H_4\mathrm{SiMe_3}$); ^{13}C-{^{1}H} NMR $(\mathrm{CDCl_3})$ δ −1.02 $(\mathrm{SiMe_3})$, 25.2 $(\mathrm{O_2C}C\mathrm{H_3})$, 51.1, 51.8 $(Me\mathrm{O_2CC{\equiv}CCO_2}Me)$, 112.21 (C_{ipso}), 105.2, 112.0, 119.4, 122.4 $(C_5\mathrm{H_4SiMe_3})$, 141.9, 154.6 $(\mathrm{MeO_2C}C{\equiv}C\mathrm{CO_2Me})$, 171.5, 171.9 $(\mathrm{MeO_2}C\mathrm{C{\equiv}C}C\mathrm{O_2Me})$ and 177.0 $(\mathrm{O_2}C\mathrm{CH_3})$.

Complex **15**: IR (Nujol) $\nu_{\mathrm{asym}}(\mathrm{CO_2^-})$ 1620, $\nu_{\mathrm{sym}}(\mathrm{CO_2^-})$ 1435, ν(C=N) 2088, 1893 $\mathrm{cm^{-1}}$, ^{1}H NMR $(\mathrm{C_6D_6})$ δ 0.09 (s, 9 H, $\mathrm{SiMe_3}$), 1.24 (s, 9 H, $\mathrm{CNBu^t}$), 1.88 (s, 3 H, $\mathrm{O_2CCH_3}$), 4.84 (2 H), 4.97 (2 H), 5.17 (2 H), 5.69 (2 H, m, $\mathrm{C_5}H_4\mathrm{SiMe_3}$); ^{13}C-{^{1}H} NMR $(\mathrm{C_6D_6})$ δ 0.32 $(\mathrm{SiMe_3})$, 25.0 $(\mathrm{O_2C}C\mathrm{H_3})$, 30.5 $[(C\mathrm{H_3})_3\mathrm{CNC}]$, 59.9 $[(\mathrm{CH_3})_3C\mathrm{NC}]$, 94.2 (C_{ipso}), 96.3, 110.3, 103.1, 108.7 $(C_5\mathrm{H_4SiMe_3})$, 177.5 $(\mathrm{O_2}C\mathrm{CH_3})$ and 213.9 $[(\mathrm{CH_3})_3\mathrm{CN}C]$.

Complex **16**: IR (Nujol) $\nu_{\mathrm{asym}}(\mathrm{CO_2^-})$ 1617, $\nu_{\mathrm{sym}}(\mathrm{CO_2^-})$ 1438, ν(CO) 1917 $\mathrm{cm^{-1}}$; ^{1}H NMR $(\mathrm{C_6D_6})$ δ 0.13 (s, 18 H, $\mathrm{SiMe_3}$), 1.84 (s, 3 H, $\mathrm{O_2CCH_3}$), 4.79 (2 H), 5.05 (4 H), 5.23 (2 H, m, $\mathrm{C_5H_4SiMe_3}$); ^{13}C-{^{1}H} NMR $(\mathrm{C_6D_6})$ δ 0.08 $(\mathrm{SiMe_3})$, 24.5 $(\mathrm{O_2C}C\mathrm{H_3})$, 97.6 (C_{ipso}), 94.9, 103.3, 105.2, 105.0 $(C_5\mathrm{H_4SiMe_3})$, 177.1 $(\mathrm{O_2}C\mathrm{CH_3})$ and 254.1 (CO).

Complex **17**: IR (Nujol) $\nu_{\mathrm{asym}}(\mathrm{CO_2^-})$ 1642, $\nu_{\mathrm{sym}}(\mathrm{CO_2^-})$ 1435, ν(C=N) 1580 $\mathrm{cm^{-1}}$; ^{1}H NMR $(\mathrm{CDCl_3})$ δ 0.06, 0.13 (s, 9 H, $\mathrm{SiMe_3}$), 1.10 (t, 3 H, $\mathrm{CH_2C}H_3$), 2.01 (s, 3 H, $\mathrm{O_2CCH_3}$), 2.40 (q, 2 H, $\mathrm{C}H_2\mathrm{CH_3}$), 5.20 (dd, 1 H, $\mathrm{PhNCC}H\mathrm{PhEt}$), 5.67 (1 H), 6.32 (1 H), 6.38 (1 H), 6.72 (1 H), 6.76 (1 H), 6.85 (1 H), 6.91 (1 H), 6.99 (1 H, m, $\mathrm{C_5}H_4\mathrm{SiMe_3}$) and 7.50–8.00 (Ph); ^{13}C-{^{1}H} NMR $(\mathrm{CDCl_3})$ δ 0.87 $(\mathrm{SiMe_3})$ 12.1 $(\mathrm{CH_2}C\mathrm{H_3})$, 25.2 $(C\mathrm{H_2CH_3})$, 26.7 $(\mathrm{O_2C}C\mathrm{H_3})$, 57.0 $(\mathrm{PhNC}C\mathrm{HPhEt})$, 108.0, 108.6, 108.7, 110.5, 110.7, 111.4, 111.7, 121.4, 124.8 $(C_5\mathrm{H_4SiMe_3})$, 124–130 (Ph), 138.32, 139.23 ($\mathrm{C^1}$ of Ph), 177.3 $(\mathrm{O_2}C\mathrm{CH_3})$ and 221 $(\mathrm{PhN}C\mathrm{CHPhEt})$.

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