for both the terminal carbonyl ν(CO) and the moderately intense carboxylate ν(OCO) regions (Table I) establish the relative concentrations of $Cp(CO)_2Ru/Cp(^{13}CO)(CO)Ru$ and $Ru(CO_2)Zr/Ru(^{13}CO_2)Zr$ groups, ^1H NMR spectra indicate the absence of other products (particularly $Cp(CO)_2RuH$), and ^{13}C NMR spectra additionally demonstrate the presence of the ^{13}C label at both the carboxylate and terminal carbonyl sites (ca. 1:1). This 1:1.3 mixture of **5a**/**5b** was used to generate the remaining μ-methyleneoxo isotopomer $Cp(CO)_2Ru(^{13}CH_2O)Zr(Cl)Cp_2$ (**7b**).

$Cp_2Zr(H)Cl$ (2 equiv) reduces **5a**/**5b** to the anticipated 1:3 mixture of **7b**/**7a** (Scheme III). Salient spectral data for **7b** appear in Table I; the same value for the methylene $^1J_{CH}$ (154 Hz) was determined by ^1H NMR spectroscopy (100 and 200 MHz). With the availability of spectral data for the three $(\mu\text{-}CO_2)RuZr$ isomers **5**, **5a**, and **5b** and for the three (μ-formaldehyde)RuZr isomers **7**, **7a**, and **7b**, we conclude that our apparent "CO_2 reduction" of $Cp(CO)_2Ru(CO_2)Zr(Cl)Cp_2$ (**5**) by $Cp_2Zr(H)Cl$ (Scheme I) engenders reduction of ligated carbon monoxide and not hydride delivery to the carboxylate (CO_2) ligand. Studies in progress focus on optimizing the choice organometallic systems L_xM and L_yM' in **1** and **2** for coupling CO_2 reduction with CO_2 insertion into metal–metal bonds.

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Easy Route for the Synthesis of Iminoacyl Niobocene Complexes. The First X-ray Structure of an (η^2-Iminoacyl)niobium Complex, $\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,N)\text{-}EtPhHCCNPh\}^+BF_4^-$

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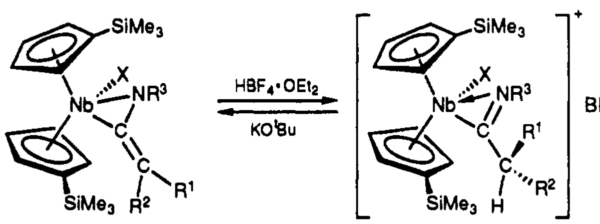
Summary: $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1R^2CCNR^3$ (X = Cl, Br) species react with 1 equiv of $HBF_4\cdot OEt_2$ to yield in one step the ionic iminoacyl complexes $\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1R^2HCCNR^3\}^+BF_4^-$. The electrochemical and the chemical reductions (Na/Hg) of these cationic complexes give the starting ketenimine complexes with the elimination of H_2. The molecular structure of $\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}EtPhHCCNPh\}^+BF_4^-$ shows an η^2(C,N)-bonded iminoacyl ligand.

Although several extensive studies have been reported on the spectroscopic and structural properties of the group 4 metal η^2-iminoacyl derivatives,[1] the study of analogous 5 metal species has been much less thorough; indeed, it is practically restricted to tantalum complexes containing ancillary aryloxide ligands[2] and to a few niobocene complexes prepared by some of us.[3]

Our studies on substituted niobocene complexes have made available to us a series of niobocene compounds containing the ketenimine group.[4] Thus, we decided to try a route for the synthesis of η^2-iminoacyl niobocene complexes based on the electrophilic attack at the free terminus of the complexed ketenimine ligands.

We report herein our initial observations, which include (i) the discovery of facile protonation of coordinated ketenimine in niobocene complexes to give iminoacyl complexes and (ii) the first X-ray structure of an (η^2-iminoacyl)niobium complex.

Red THF solutions of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1R^2CCNR^3)$ react at room temperature with 1 equiv of $HBF_4\cdot OEt_2$ to give, through a protonation process, white solids corresponding to the η^2-iminoacyl complexes $\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\eta^2(C,N)\text{-}R^1R^2HCCNR^3\}^+BF_4^-$ in essentially quantitative yield (eq 1).



(1)

1–4

1: X = Cl, $R^1 = R^2 = R^3 = C_6H_5$
2: X = Br, $R^1 = R^2 = R^3 = C_6H_5$
3: X = Cl, $R^1 = C_6H_5$, $R^2 = C_2H_5$, $R^3 = C_6H_5$
4: X = Br, $R^1 = C_6H_5$, $R^2 = C_2H_5$, $R^3 = C_6H_5$

† Universidad de Castilla-La Mancha.
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(1) (a) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209. (b) Treichel, P. M. *Adv. Organomet. Chem.* **1983**, *11*, 21. (c) Lappert, M. F.; Luong-Thi, N. T.; Milne, C. R. *J. Organomet. Chem.* **1979**, *174*, C35. (d) Reger, D. L.; Tarquini, M. K.; Lebioda, L. *Organometallics* **1983**, *2*, 1763. (e) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 2928.
(2) (a) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390. (b) McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1072. (c) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 1986. (d) Chamberlain, L. R.; Rothwell, I. P.; Huffmann, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1023.
(3) Martinez de Ilarduya, J. M.; Otero, A.; Royo, P. *J. Organomet. Chem.* **1988**, *340*, 187.

0276-7333/91/2310-3435$02.50/0

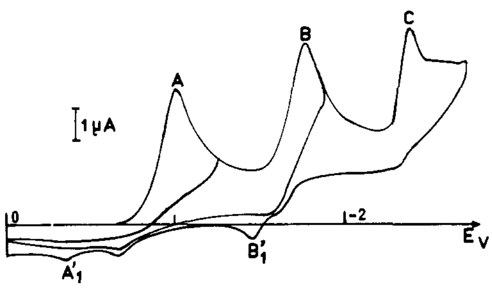


Figure 1. Cyclic voltammogram of {Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2-(*C*,*N*)-$Ph_2HCCNPh$)}$^+BF_4^-$ in tetrahydrofuran at a platinum-disk working electrode (starting potential 0 V, sweep rate 0.2 V s^{-1}). Potentials are in volts relative to a saturated calomel electrode.

Workup by crystallization (mixture of dichloromethane–hexane) afforded colorless air-stable crystals of iminoacyl niobocene complexes.

A facile H^+ abstraction occurs when the iminoacyl complexes are reacted with 1 equiv of KO^{t}Bu to give the initial ketenimine complexes (eq 1).

In THF at a platinum electrode with 0.2 M tetrabutylammonium hexafluorophosphate as supporting salt the polarogram of compound 1 shows the three reduction waves A–C (A, $E_{1/2}$ = −0.94 V; B, $E_{1/2}$ = −1.75 V; C, $E_{1/2}$ = −2.4 V; versus SCE).

Also in THF as solvent at a platinum electrode, the cyclic voltammogram of complex 1 exhibits the corresponding peaks A–C. On the reverse scan after peak C the two oxidation peaks B'_1 and A'_1 appear (Figure 1) in the voltammogram. After an exhaustive electrolysis of the derivative at −1.2 V (plateau of wave A) at room temperature and a consumption of a quantity of electricity near 1 equiv of electrons, a red solution was obtained, from which after appropriate workup the starting ketenimine complex was isolated. On the other hand, the cyclic voltammogram of the electrolyzed solution was similar to that of the starting ketenimine complex, which was reducible[4] at the potential of peak B.

The above results agree with the reaction

$$\{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,N)\text{-}Ph_2HC{-}C{=}NPh)\}^+ \rightarrow$$
$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2(C,N)\text{-}Ph_2C{=}C{=}NPh) + \tfrac{1}{2}H_2 \quad (2)$$

We chose also to investigate the reduction of the complexes 1–4 with 1 equiv of Na/Hg. A mixture of the iminoacyl complex and Na/Hg in THF reacts at room temperature to give a red solution, from which the starting ketenimine was isolated. H_2 was also detected by a GC analysis of the gaseous phase.

The complexes 1–4 prepared in this study contain the iminoacyl function both carbon and nitrogen bound in an η^2 fashion. This is based on the observed solid-state structure of one of the derivatives combined with the similarity of their spectroscopic properties.

In fact, in order to gain more insight into the structural aspects of the η^2 coordination of the iminoacyl group in our complexes, a single-crystal X-ray structure determination was carried out on complex 3 (Figure 2). This complex has a bent-sandwich structure[5] related to those of the most widely studied η^2-acyl and η^2-iminoacyl derivatives of the group 4 metals, namely those of formula $MCp_2(\eta^2\text{-}R^1CX)$ (M = Ti, Zr, Hf; X = O, NR^2).[6] As far as we know, this structure represents the first example reported of an (iminoacyl)niobium complex. The Nb–N and Nb–C(1) distances of 2.148 (5) and 2.170 (5) Å, respectively, are characteristic of the iminoacyl function. The N–C(1), C(1)–N, Nb–N, and Nb–Cl vectors are practically coplanar in the plane bisecting the metallocene unit.

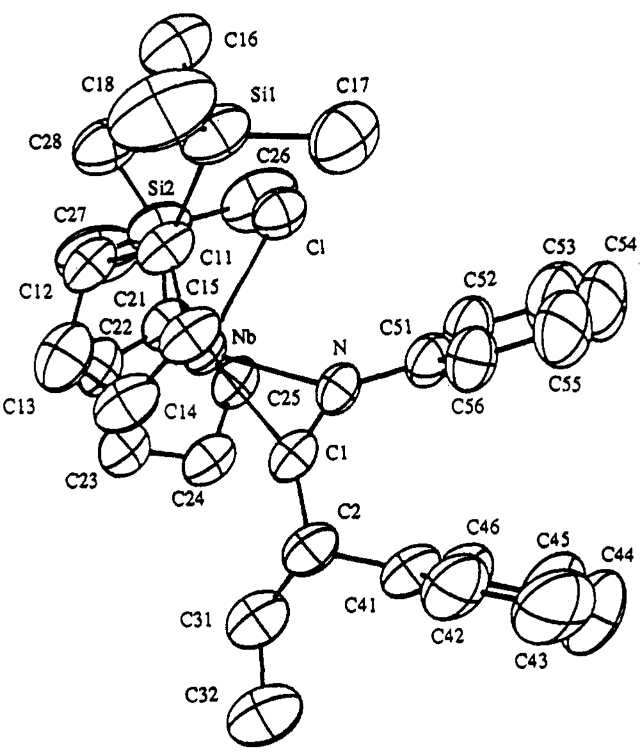


Figure 2. Structure of the cation in {Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2-(*C*,*N*)-EtPhHCCNbc)}$^+BF_4^-$. CP denotes the gravity centers of cyclopentadienyl rings. Selected bond distances (Å) and angles (deg): Nb–Cl, 2.468 (2); Nb–N, 2.148 (5); Nb–C(1), 2.170 (5); N–C(1), 1.23 (1); C(1)–C(2), 1.51 (1); Nb–CP(1), 2.116; Nb–CP(2), 2.110; Cl–Nb–N, 80.4 (2); Cl–Nb–C(1), 113.5 (3); N–Nb–C(1), 33.2 (4); CP(1)–Nb–CP(2), 130.1.

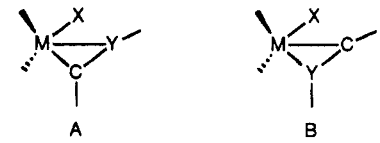
(4) Antiñolo, A.; Fajardo, M.; López-Mardomingo, C.; Otero, A.; Mourad, Y.; Mugnier, Y.; Sanz-Aparicio, J.; Fonseca, I.; Florencio, F. *Organometallics* **1990**, *9*, 1919.

(5) Crystallographic data for 3: monoclinic, space group *C*2/*c* (No. 15), *a* = 23.962 (8) Å, *b* = 21.408 (5) Å, *c* = 15.456 (3) Å, β = 123.30 (2)°, *V* = 7055.5 Å^3, d_{calc} = 1.368 g cm^{-3}, *Z* = 8, and μ = 4.76 cm^{-1}. A colorless crystal having the approximate dimensions 0.4 × 0.25 × 0.15 mm was used for data collection, carried out at 296 (1) K on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.71073 Å). Intensity data were collected for 5856 reflections. The Enraf-Nonius CAD4-SDP library was used for data reductions, and the solution and refinement of the structure were performed with SHELX76 programs. Full-matrix least-squares refinement of 3197 unique reflections with $I > 3\sigma(I)$ converged at *R* = 0.046, R_w = 0.048, and GOF = 1.871. The structure is made up of discrete organometallic cations and BF_4^- anions. All non-hydrogen atoms in the cation were refined with anisotropic temperature factors, but isotropic factors were applied to the atoms in BF_4^-. Hydrogen atoms were placed in calculated positions. Three of the four fluorine atoms in BF_4^- are disordered and were refined with occupancies equal to 0.5. The mean B–F distances (1.37 Å) and F–B–F angles (109.5°) are normal. One could suppose that the disorder of BF_4^- anions affects the cation because some carbon atoms of the phenyl groups (C(43), C(44), C(45), C(53), and C(54)) have rather high temperature factors (supplementary material). However, this is not evident, because the short fluorine–carbon distances from 3.15 to 3.81 Å are associated with the carbon atoms with normal temperature factors, while the shortest fluorine–carbon distance with a high temperature factor (F(21)–C(43)) is equal to 3.82 Å. Complete details of the data collection and refinement are available as supplementary material.

(6) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733.

The most notable characteristic of the NMR spectra[7] is the position of the resonance for the η^2-CNR^3 carbon atom, which was found to resonate between δ 209.7 and 215.7, in accord with data previously reported for other η^2-iminoacyl derivatives of early transition metals.[1-3]

Chart I



Y = O, N

η^2-Acyl and -iminoacyl metallocenes have been found[1c] to adopt two possible structures (Chart I). Although it has been demonstrated[8] that isomer B is the resulting initial kinetic product of the insertion reaction, the majority of group 4 metal derivatives show the structure A.[9] In our complex we have found the ground-state structure A with the bulky fragment away from the halogen atom.

Investigations to explore both the scope of the method to prepare related compounds and the reactivity of iminoacyl complexes are in progress.

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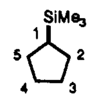
Supplementary Material Available: Text describing experimental procedures, a table giving details on the X-ray structure analysis, and tables of positional parameters for non-hydrogen atoms, anisotropic thermal parameters, interatomic distances and angles, least-squares planes, and hydrogen atom positions (13 pages); a listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

(7) The main spectroscopic data for η^2-iminoacyl complexes are as follows.



1: IR (Nujol) ν(C=N) 1717 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.04 (s, 18 H, $SiMe_3$), 5.83 (4 H), 6.18 (4 H), (each a complex signal, C_5H_4), 6.56 (s, 1 H, C*H*Ph_2, 7.00–7.20 (m, 15 H, *Ph*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −0.5 (Si*Me*$_3$), 58.4 (Ph_2*C*H), 114.4 (C^1), 108.7, 109.9, 122.5, 124.4 (C^2, C^3, C^4, C^5; exact assignment not possible), 128.4, 128.6, 128.8, 129.3, 129.3, 129.4, 132.2 (*C* of phenyl groups), 135.7, 136.2 (C_{ipso} of phenyl groups), 213.6 (*C*=N). Anal. Found (calcd for $C_{36}H_{42}BClF_4NNbSi_2$): C, 55.99 (56.89); H, 5.34 (5.57); N, 1.72 (1.84). **2**: IR (Nujol) ν(C=N) 1716 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 18 H, Si*Me*$_3$), 6.18 (2 H), 6.34 (2 H), 6.42 (2 H), 6.94 (2 H) (each a complex signal, C_5H_4), 6.78 (s, 1 H, C*H*Ph_2), 7.20–7.40 (m, 15 H, *Ph*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 0.04 (Si*Me*$_3$), 57.9 (Ph_2*C*H), 116.2 (C^1), 107.6, 110.3, 124.3, 125.2 (C^2, C^3, C^4, C^5; exact assignment not possible), 128.7, 128.8, 128.9, 129.0, 129.4, 129.6, (*C* of phenyl groups), 135.9, 135.8 (C_{ipso} of phenyl groups), 209.7 (*C*=N). Anal. Found (calcd for $C_{36}H_{42}BBrF_4NNbSi_2$): C, 53.70 (53.74); H, 5.56 (5.26); N, 1.64 (1.74). **3**: IR (Nujol) ν(C=N) 1707 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H, Si*Me*$_3$), 0.21 (s, 9 H, Si*Me*$_3$) (two different signals for the $C_5H_4SiMe_3$ diastereotopic species), 1.01 (t, 3 H, CH_3, J = 7.0 Hz), 2.38 (m, 2 H, $CHCH_AH_BCH_3$), 5.05 (dd, 1 H, $CHCH_AH_B$, J = 4.4 Hz, J = 10.9 Hz), 5.92 (1 H), 5.97 (1 H), 6.04 (1 H), 6.16 (1 H), 6.43 (3 H), 6.72 (1 H) (each a complex signal, C_5H_4), 7.15–7.60 (m, 10 H, *Ph*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −0.34 (Si*Me*$_3$), 11.9 ($CHCH_2CH_3$), 27.1 ($CHCH_2CH_3$), 55.3 (PhEt*C*H), 108.3, 108.5, 109.8, 111.4, 115.1, 115.7, 122.5, 123.3, 124.0, 124.0 (C^1, C^2, C^3, C^4, C^5; for the two $C_5H_4SiMe_3$ diastereotopic species, exact assignment not possible), 128.7, 128.8, 128.9, 129.1, 129.4, 129.7, (*C* of phenyl groups), 135.9, 136.1 (C_{ipso} of phenyl groups), 215.7 (*C*=N). Anal. Found (calcd for $C_{32}H_{42}BClF_4NNbSi_2$): C, 53.86 (53.98); H, 6.33 (5.94); N, 1.97 (1.94). **4**: IR (Nujol) ν(C=N) 1689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9 H, Si*Me*$_3$), 0.21 (s, 9 H, Si*Me*$_3$) (two different signals for the $C_5H_4SiMe_3$ diastereotopic species), 0.97 (t, 3 H, CH_3, J = 7.1 Hz), 2.16 (m, 1 H, $CHCH_AH_BCH_3$), 2.32 (m, 1 H, $CHCH_AH_BCH_3$), 5.06 (dd, 1 H, $CHCH_AH_BCH_3$, J = 4.8 Hz, J = 10.1 Hz), 5.93 (1 H), 6.01 (1 H), 6.05 (2 H), 6.38 (1 H), 6.49 (2 H), 6.63 (1 H) (each a complex signal, C_5H_4), 7.15–7.40 (m, 10 H, *Ph*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 0.1 (Si*Me*$_3$), 12.0 ($CHCH_2CH_3$), 27.3 ($CHCH_2CH_3$), 54.9 (PhEt*C*H), 106.9, 107.7, 110.7, 110.9, 116.9, 116.9, 117.5, 123.9, 124.2, 124.8 (C^1, C^2, C^3, C^4, C^5; for the two $C_5H_4SiMe_3$ diastereotopic species, exact assignment not possible), 128.9, 129.1, 129.3, 129.9 (*C* of phenyl groups), 135.6, 136.3 (C_{ipso} of phenyl groups), 211.9 (*C*=N). Anal. Found (calcd for $C_{32}H_{42}BBrF_4NNbSi_2$): C, 50.78 (50.81); H, 5.86 (5.59); N, 1.71 (1.85).

(8) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

(9) Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297.