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Insertion reactions of heterocumulenes into the niobium-hydride bond of isocvanide and carbonyl niobocene complexes

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Abstract

The reaction of the hydride niobocene complexes, Nb(η^{5} -C₅H₄SiMe₃)₂(H)(CNR) (R = 2,6-dimethylphenyl (Xylyl) or cyclohexyl (Cy)) and Nb(η^{5} -C₅H₄SiMe₃)₂(H)(CO) with the heterocumulenes PhN=C=X (X=O or S) affords the new formamido and thioformamido complexes Nb(π^{1} -C₄H₄SiMe₃)₂(CNR)(π^{1} -XC(H)NPh) (R=Xylyl, X=O (1); R=Xylyl, X=S (2); R=Cy, X=O (3); R=Cy, X=S (2) (4)) and Nb(η^{5} -C₁H₄SiMe₃)₂(CO)(η^{1} -XC(H)NPh) (X = O (5); X = S (6)). The protonation of these derivatives using HCF₃COO yields the trifluoroacetato complexes Nb(η^5 -C₅H₄SiMe₃)₂(CNR)(η^1 -OOCCF₃) (R = Xylyl (7); R = Cy (8)) and Nb(η^5 -C₅H₄SiMe₃)₂(CO)(η^1 -OOCCF₁) (9) and the imine derivatives HOC(H)=NPh and HSC(H)=NPh. Thermal treatment of 5 gives the η^2 -formamido complex Nb(η^5 -C₅H₄SiMe₃)₂(η^2 -OC(H)NPh) (10). All these complexes have been characterised by spectroscopic methods.

Keywords: Insertion reactions; Heterocumulenes; Niobium complexes; Niobocene complexes; Hydride complexes; Isocyanide complexes; Carbonyl complexes

1. Introduction

Hydride complexes of transition metals represent one of the most important classes of compounds due to their chemical reactivity and importance in catalysis [1]. In this field insertions of unsaturated molecules into the metal-hydride bond are considered as fundamental chemical steps in several catalytic cycles and frequently lead to reactive intermediates [2]. Thus in connection with our studies of metal-promoted activation of heterocumulenes, such as ketene and ketenimine, with niobocene complexes [3], we have recently studied the insertion processes of the niobium-hydride bond of several niobocene derivatives of carbon disulfide [4], carbon dioxide [5] and activated alkynes [6] which has allowed the preparation of thioformato, formato and alkenyl derivatives, respectively. These results encouraged us to explore the reactivity of the niobium-hydride bond with other heterocumulenes such as isocyanate and isothiocyanate whose metal-activation processes by the sixteen-electron species Nb(η^5 -C₅H₄SiMe₃)₂Cl have been previously described [7]. This paper will focus on the synthesis of new formamido and

thioformamido niobocene complexes and the study of their protonation with trifluoroacetic acid.

2. Experimental

2.1. 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. The complexes Nb(η^{5} -C₅H₄SiMe₃)₂(H)(CN(C₆H₃- $(Me)_{2}, 2, 6), Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(H)(CNC_{6}H_{11})$ [8] and Nb(η^5 -C₅H₄SiMe₃)₂(H)(CO) [9] were prepared as described earlier. HCF3COO was purchased from Fluka and used without further purification. PhNCO and PhNCS were purchased from Aldrich and distilled before use. IR spectra were recorded on a Perkin-Elmer PE 883 IR spectrophotometer. ¹H and ¹³C spectra were recorded on Varian FT-300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuteriated solvent. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyser.

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2.2. $Nb(\eta^5 - C_5 H_4 SiMe_3)_2(CNR)(\eta^1 - XC(H_3)NPh) (R = Xylyl, X = O (1); R = Xylyl, X = S (2); R = Cy, X = O (3); R = Cy, X = S (4))$

The isocyanate, PhNCO (0.164 ml, 1.20 mmol), was added to a solution of Nb(η^5 -C₃H₄SiMe₃)₂(H)(CN(2,6-(Me)₂·(C₆H₃)) (0.60 g, 1.20 mmol) in THF (~50 ml). The resulting mixture was stirred for 30 min at room temperature and the solvent was removed in vacuo to give a green oily solid which was washed with cold hexane (20 ml at -30° C) to yield the green solid 1 (0.66 g, 88%). 2-4 were prepared in a similar manner to 1 (80–90% yields).

1: IR (Nujol): ν (CNR) 2038, ν (C=N) 1623 cm⁻¹. ¹H NMR (200 MHz, C₂D₆): δ 0.21 (s, 18H, SiMe₃), 4.83 (2H), 5.18 (2H), 5.51 (2H), 5.83 (2H) (m, C₃H₄), 1.89 (s, 6H, Me-CNR), 6.66 (m, 3H, C₆H₃-CNR), 8.37 (s, 1H, N=C-H). ¹³C{¹H} NMR (300 MHz, C₆D₆): δ 0.32 (SiMe₃), 95.17, 97.23 (C¹), 98.61, 106.16, 108.50 (C₃H₄), 18.78 (Me-CNR), 252.97 (CNR), 170.90 (N=C-H). ¹³C NMR (300 MHz, C₆D₆): ¹J(C-H) 160.27 Hz. Anal. Calc. for C₃₂H₄1N₂NbOSi₂: C, 62.12; H, 6.68; N, 4.53. Found: C, 61.99; H, 6.58; N, 4.46%.

2: IR (Nujol): ν (CNR) 2045, ν (C=N) 1597 cm⁻¹. ¹H NMR (200 MHz, C₂D₆): δ 0.10 (s, 18H, SiMe₃), 4.99 (2H), 5.03 (2H), 5.42 (2H), 5.57 (2H) (m, C₃H₄), 2.55 (s, 6H, Me-CNR), 6.77 (m, 3H, C₆H₃-CNR), 9.14 (s, 1H, N=C-H). ¹³C{¹H} NMR (300 MHz, C₂D₆): δ 0.45 (SiMe₃), 94.75, 98.45 (C¹), 100.46, 103.61, 104.51 (C₃H₄), 19.40 (Me-CNR), 217.11 (CNR), 173.70 (N=C-H). ¹³C NMR (300 MHz, C₆D₆): ¹J(C-H) 164.30 Hz. Anal. Calc. for C₃₂H₄₁N₂NbSSi₂: C, 60.54; H, 6.51; N, 4.41. Found: C, 60.76; H, 6.54; N, 4.54%.

3: IR (Nujol): ν (CNR) 2034, ν (C=N) 1645 cm⁻¹. ¹H NMR (200 MHz, C₂D₆): δ 0.24 (s, 18H, SiMe₃), 4.73 (2H), 5.04 (2H), 5.49 (2H), 5.75 (2H) (m, C₅H₄), 0.91–1.43, 3.00 (m, 11H, CNC₆H₁), 8.26 (s, 1H, N=C-H). ¹³C(¹H) NMR (300 MHz, C₂D₆): δ 0.74 (SiMe₃), 93.01, 94.61, 95.40 (C¹), 97.25, 99.19 (C₅H₄), 23.24, 24.78, 26.92, 35.01, 57.06 (C¹), 67.69 (CNC₆H₁₁), 252.50 (CNC₆H₁₁), 171.03 (N=C-H). ¹³C NMR (300 MHz, C₆D₆): ¹/(C-H) 166.42 Hz. Anal. Calc. for C₃₀H₄₃N₂NbOSi₂: C, 60.38; H, 7.26; N, 4.69. Found: C, 60.35; H, 7.30; N, 4.62%.

4: IR (Nujol): ν (CNR) 2096, ν (C=N) 1593 cm⁻¹. ¹H NMR (200 MHz, C₆D₆): δ 0.16 (s, 18H, SiMe₅), 4.86 (2H), 4.93 (2H), 5.42 (2H), 5.51 (2H) (m, C₅H₄), 0.83–1.60, 3.24 (m, 11H, CNC₆H₁), 9.20 (s, 1H, N=C-H). ¹¹C(¹H] NMR (300 MHz, C₆D₆): δ 0.99 (SiMe₃), 90.00 (C¹), 94.51, 100.81, 103.26, 104.70 (C₅H₄), 24.54, 25.73, 26.17, 34.02, 59.02 (C¹), 68.21 (CNC₆H₁₁), 254.53 (CNC₆H₁₁), 175.34 (N=C-H). ¹³C NMR (300 MHz, C₆D₅): 1 (C-H) 170.0i Hz. Anal. Calc. for C₃₀H₄₃N₂NDOSi₂: C, 58.80; H, 7.07; N, 4.57. Found: C, 58.53; H, 6.97; N, 4.48%.

2.3. $Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(CO)(\eta^{1}-XC(H)NPh) (X = O(5); X = S(6))$

5 and 6 were prepared in a similar manner to 1 in yields of 80-90%.

5: IR (Nujol): ν (CO) 1937, ν (C=N) 1619 cm⁻¹. ¹H NMR (200 MHz, C₆D₆): δ 0.09 (s, 18H, SiMe₅), 4.65 (2H), 4.79 (2H), 5.38 (2H), 5.51 (2H) (m, C₅H₄), 8.19 (s, 1H, N=C-H). ¹³C(¹H) NMR (300 MHz, C₆D₆): δ -0.08 (SiMe₃), 94.88, 96.29 (C¹), 98.62, 103.50, 106.60 (C₅H₄), 253.83 (CO), 171.17 (N=C-H). ¹³C NMR (300 MHz, C₆D₆): ¹J(C-H) 167.76 Hz. *Anal.* Calc. for C₂₄H₃₂-NNbO₂Si₂: C, 55.91; H, 6.26; N, 2.72. Found: C, 55.73; H, 6.19; N, 2.78%.

6: IR (Nujol): ν (CO) 1919, ν (C=N) 1594 cm⁻¹. ¹H NMR (200 MHz, C₆D₆): δ 0.15 (s, 18H, SiMe₃), 4.77 (2H), 4.86 (2H), 4.90 (2H), 5.47 (2H) (m, C₅H₄), 8.96 (s, 1H, N=C-H). ¹³Cl¹H) NMR (300 MHz, C₆D₆): δ 0.19 (SiMe₃), 94.35, 95.10 (C¹), 97.99, 105.04, 105.30 (C₅H₄), 255.62 (CO), 172.09 (N=C-H). ¹³C NMR (300 MHz, C₆D₆): ¹J(C-H) i59.85 Hz. *Anal.* Calc. for C₃₄H₃₂-NNbOSSi₂: C, 54.22; H, 6.07; N, 2.63. Found: C, 54.40; H, 6.14; N, 2.71%.

2.4. $Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(CN(2,6-(Me)_{2}-(C_{6}H_{3})-(\eta^{1}-OOCCF_{3})(7))$

 $HCF_3COO\left(0.082\,ml, 1.07\,mmol\right)$ was added to a solution of $Nb(\eta^2-C_5H_3)iMc_3)_2(CN(2,6-(Me)_2-(C_6H_3)(\eta^2-OC-(H)NPh)$ (1) (0.66 g, 1.07 mmol) in THF (\sim 50 ml) at -78° C. The resulting solution was allowed to warm to room temperature whilst stirring for 2 h. The solvent was removed in vacuo to give a purple oily solid which was washed with cold hexane (20 ml at -30° C) to yield the purple solid 7 (0.48 g, 74%). The title complex was also prepared using compound 2 instead of 1.

7: IR (Nujol): ν (CNR) 2075, ν_{asym} (CO₂⁻) 1670, ν_{sym} (CO₂⁻) 1405, Δ = 265 cm⁻¹, ¹H NMR (200 MHz, C₆C₆): δ - 0.02 (s, 18H, SiMe₃), 4.62 (2H), 4.77 (2H), 5.03 (2H), 5.29 (2H) (m, C₃H₄), 2.16 (s, 6H, *Me*-CNR), 6.42 (m, 3H, C₆H₂-CNR). ¹³C(¹H) NMR (300 MHz, C₆D₆): δ 0.32 (SiMe₃), 95.41, 96.70 (C¹), 98.98, 100.47, 104.31 (C₅H₄), 192.30 (O₂CCF₃), 163.41 (O₂CCF₃) (¹J(C-F) 58.04 Hz), 242.17 (CNR). *anal.* Calc. for C₂₇H₃₅F₃NNbO₂Si₂: C, 53.02; H, 5.77; N, 2.29. Found: C, 53.12; H, 5.89; N, 2.20%.

2.5. $Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(CNC_{6}H_{11})(\eta^{1}-OOCCF_{3})$ (8)

8 was prepared in a similar manner to 7 from the reaction of 3 or 4 with HCF₃COO (yield 68%).

8: IR (Nujol): ν(CNR) 2041, $ν_{asym}(CO_2^{-})$ 1645, $ν_{sym}(CO_2^{-})$ 1408, $\Delta = 237$ cm⁻¹. ¹H NMR (200 MHz, C₆D₆): $\delta - 0.03$ (s, 18H, SiMe₃), 4.54 (2H), 4.63 (2H), 4.97 (2H), 5.38 (2H) (m, C₅H₄), 0.83–1.80, 3.84 (m, 11H, CNC₆H₁). ¹³C{¹H} NMR (300 MHz. C₆D₆): $\delta 0.49$ (SiMe₃), 92.41 (C¹), 94.49, 99.99, 100.37, 106.42 (C₅H₄), 24.13, 25.25, 33.55, 38.01, 56.50 (C¹), 68.04 (CNC₆H₁), 190.24 (O₂CCF₃), 162.10 (O₂CCF₃) (¹J(C-F) 53.24 Hz), 243.78 (CNC₆H₁₁). Anal. Calc. for C₂₅H₃₇F₃NhbO₂Si₂: C, 50.92; H, 6.32; N, 2.38. Found: C, 50.70; H, 6.21; N, 2.29%.

2.6. $Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(CO)(\eta^{1}-OOCCF_{3})(9)$

9 was prepared in a similar manner to 7 from the reaction of 5 or 6 with HCF_3COO (yield 71%).

9: IR (Nujol): ν (CO) 1946, ν_{asym} (CO₂⁻) 1688, ν_{sym} (CO₂⁻) 1403, $\Delta = 285$ cm⁻¹. ¹H NMR (200 MHz, C₆D₆): $\delta = 0.05$ (s, 18H, SiMe₃), 4.71 (2H), 4.96 (2H), 5.05 (2H), 5.12 (2H) (m, C₅H₄). ¹³C(¹H) NMR (300 MHz, C₆D₆): $\delta 0.21$ (SiMe₃), 97.21 (C¹), 100.41, 105.00, 105.09, 107.23 (C₅H₄), 195.23 (O₂CCF₃), 164.81 (O₂CCF₃) (¹J(C-F) 60.17 Hz), 253.18 (CO). Anal. Calc. for C₁₉H₂₆F₃NbO₃Si₂: C, 44.88; H, 5.15. Found: C, 44.95; H, 5.14%.

HOC(H)=NPh: ¹H NMR (200 MHz, C_6D_6): δ 7.70 (d, 1H, HO-CH=NPh), 9.45 (d, 1H, HO-CH=NPh) (³J('H-¹H) 8.02 Hz), 7.02 (m, 5H, HO-CH=NPh). ¹³C['H] NMR (300 MHz, C_6D_6): δ 110.41 (C¹), 115.25, 122.34, 123.32, 130.41, 137.21 (HO-CH=NPh), 168.60 (HO-CH=NPh).

HSC(H)=NPh: ¹H NMR (200 MHz, C₆D₆): δ 7.20 (d, 1H, HS-CH=NPh), 9.90 (d, 1H, HS-CH=NPh) (³/(¹H-¹H) 7.97 Hz), 6.94 (m, 5H, HS-CH=NPh). ¹³C{¹H} NMR (300 MHz, C₆D₆): δ 108.51 (C¹), 114.48, 120.24, 122.28, 129.69, 138.82 (HS-CH=NPh), 164.12 (HS-CH=NPh).

2.7. $Nb(\eta^{5}-C_{5}H_{4}SiMe_{3})_{2}(\eta^{2}-OC(H)NPh)$ (10)

A solution of Nb(η^5 -C₃H₄SiMe₃)₂(CO)(η^1 -OC(H)-NPh) (5) (0.50 g, 0.97 mmol) in toluene (~50 ml) was refluxed for 10 h. The solvent was removed in vacuo to give a brown oily solid which was washed with cold hexane (20 ml at -30° C) to yield the brown solid 10 (0.32 g, 83%).

10: IR (Nujol): $\nu(\eta^2-0=CH=NPh)$ 1552 cm⁻¹. ¹H NMR (200 MHz, C₆D₆): δ 0.01 (s, 18H, SiMe₃), 4.36 (2H), 4.58 (2H), 5.12 (2H), 5.97 (2H) (m, C₆H₄), 8.20 (s, 1H, O=CH=NPh). ¹³C[¹H] NMR (300 MHz, C₆D₆): δ 0.83 (SiMe₃), 95.70 (C¹), 99.47, 101.11, 104.10, 109.73 (C₅H₄), 176.01 (O=CH=NPh). Anal. Calc. for C₂₃H₃₃NNbOSi₂: C, 56.66; H, 6.61; N, 2.87. Found: C, 56.43; H, 6.54; N, 2.77%.

3. Results and discussion

We recently prepared the hydride-isocyanide niobocene complexes, Nb($\eta^5 C_3 H_4 SiMe_3$)₂(H)(CNR) (R = Xylyl or Cy) from the reaction of Nb($\eta^5 - C_3 H_4 SiMe_3$)₂(H)₃ with the appropriate isocyanide [8] and these complexes along with Nb($\eta^5 - C_3 H_4 SiMe_3$)₂(H)(CO) [9] have been used in studying the behaviour of hydride complexes with PhNCO and PhNCS.

One equivalent of PhNCO reacts smoothly with the hydride niobocene complexes Nb(η^5 -C₃H₄SiMe₃)₂(H)(L) (L=CN (Xylyl), CN (Cy) or CO) in THF at room temperature to afford the corresponding formamido niobocene complexes Nb(η^5 -C₃H₄SiMe₃)₂(CNR)(η^1 -OC(H)NPh) (R=Xylyl (1), Cy (3)) and Nb(η^5 -C₃H₄SiMe₃)₂-(CO)(η^1 -OC(H)NPh) (5) (Scheme 1).



(CNR) (η^1 -SC(H)NPh) (R=Xylyl (2), Cy (4)) and Nb-(η^2 -C₂H₂SiMe₃)₂(CO) (η^1 -OC(H)NPh) (6) (Scheme 1). The different complexes were isolated as air-sensitive solids after appropriate work-up (see Section 2). Other similar formamido and thioformamido niobium or tantalum derivatives have previously been described [10]. The structural characterisation of the new formamido and thioformamido complexes was carried out by IR and NMR spectroscopy. The IR spectra of 1–6 show a characteristic band at ~ 1600 cm⁻¹, which has been assigned to ν (C=N) of the formamide or thioformanide ligand (Scheme 2(a)), although this could alternatively correspond to ν (C=O) in an alternative structural situation for 1, 3 and 5 (Scheme 2(b)) resulting from the insertion of the N=C bond of PhNCO in the Nb-H bond.

Additionally, IR spectra show characteristic bands at $\sim 2000 \text{ cm}^{-1}$ which correspond to $\nu(C\equiv N)$ and $\nu(C\equiv O)$ of the isocyanide and carbonyl ancillary ligands, respectively. ¹H and ¹³C NMR spectra of 1–6 show four and five signals, respectively, for the cyclopentadienyl rings in accordance with a lack of symmetry in the structure of these complexes. Carbon and proton resonances for the formamide or thioformamide ligands appear at $\sim 170 (X-C(H)NPh)$ and $\sim 8.50 (X-C(H)NPh)$ ppm, respectively (see Section 2). The value or 1/(C-H) of ~ 165 Hz is significant as it is concurs with the value expected for the sp² hybridisation of the formamide or thioformamide carbon atom [11]. In addition, ¹³C NMR spectra show additional characteristic signals for the ancillary ligands, namely at ~ 230 and 250 ppm for the isocyanide and carbonyl carbon atoms bound to the niobium centre.

Protonation of 1-6 was carried out using trifluoroacetic acid as a protonating agent. When THF solutions of these



complexes were treated with stoichiometric amounts of HCF₃COO at low temperature and after 2 h of stirring, the corresponding trifluoroacetato complexes Nb(η^{5} -C₃H₄Si-Me₃)₂(L)(η^{1} -OOCCF₃) (L=CN(Xylyl) (7), CN(Cy) (8), CO (9)) and the imines HX-C(H)=NPh (X=O, S) were obtained (see Scheme 3). After appropriate work-up the different products were isolated and characterised (see Scetion 2).

In the reaction of the complexes containing isocyanide as the ancillary ligands 1-4, the protonation gave quantitatively and exclusively the aforementioned products. The alternative protonation of the nitrogen atom of the isocyanide ligand was not observed. This result contrasts with that found in the protonation of various hydride-isocyanide niobocenes, Nb(η^5 -C₅H₄SiMe₃)₂(H)(CNR) (R = Bu^t or Cy), where in addition to the major product, $[Nb(\eta^5-C_5H_4SiMe_3)_2(\eta^2-H_2)_2$ (CNR)]⁺, a minor product, resulting from the protonation of the nitrogen isocyanide atom, $[Nb(\eta^5-C_5H_4SiMe_3)_2(H)-$ (CN(H)R)]⁺, was formed [12]. 7-9 have been spectroscopically characterised. IR spectra show the characteristic bands which correspond to $\nu(C=N)$ at ~2100 cm⁻¹ in 7 and 8 and ν (C=O) at 1946 cm⁻¹ in 9. For the acetate ligand the CO2⁻ stretching frequencies are usually the most prominent feature and the normal approach has been to relate the values of Δ (the separation between $\nu_{asym}(CO_2^-)$) and $v_{sym}(CO_2^{-}))$ with the mono- or bidentate character of the ligand [13]. The IR spectra of 7-9 show two bands at ~ 1650 and 1410 cm⁻¹ which correspond to $v_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^{-})$, respectively; the value of $\Delta = 240 \text{ cm}^{-1}$ is significantly much greater than the 'ionic' value of $\Delta = 164$ cm^{-1} [13], indicating that the acetate ligand acts in these complexes as a monodentate ligand. 1H and 13C NMR spectra support this proposal; four and five signals, respectively, for the cyclopentadienyl rings confirm that an unsymmetrical structure for these complexes exists in solution (see Scheme 3). The ¹³C resonance for the acetate ligand appears at ~ 190 ppm and those for the isocyanide cart on bound to the niobium centre and the carbonyl carbon atom are observed at ~250 and 230 ppm, respectively. The isolated organic imine derivatives have also been characterised by NMR spectroscopy (see Section 2).

Finally the thermal behaviour of 5 has been studied. When a solution of 5 in toluene was refluxed, evolution of CO took place and the resulting η^2 -formamido complex Nb(η^5 -C₃H₄SiMe₃)₂(η^2 -OC(H)NPh) (10) was isolated after appropriate work-up (Scheme 4).



The IR spectrum of 10 shows a band at 1552 cm^{-1} which is indicative of a chelating formamido ligand [13]. ¹H and ¹³C NMR spectra of 10 show four and five signals, respectively, for the cyclopentadienyl rings in accordance with an unsymmetrical structure for 10. Additionally, resonances assignable to the η^2 -formamide group have also been observed in both ¹H and ¹³C NMR, the formamido hydrogen appearing at 8.2 ppm and the formamido carbon at 176.1 ppm, shifts which are comparable to those found for related formamido complexes [10a,c,14].

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References

- [1] G.G. Hlatky and R.H. Crabtree, Coord. Chem. Rev., 65 (1985) 1.
- [2] J.P. Collman, L.S. Hegedus, J.R. Norton and R.E. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.
- [3] (a) A. Antiñolo, M. Fajardo, C. López-Mardomingo, A. Otero, Y. Mourad, Y. Mugnier, J. Sanz-Aparicio, I. Fonseca and F. Florencio, Organometallics, 9 (1990) 164; (b) A. Antiñolo, A. Otero, M. Fajardo, C. López-Mardomingo, D. Lucas, Y. Mugnier, M. Lanfranchi and M.A. Pellinghelli, J. Organomet. Chem., 435 (1992) 55; (c) A. Antiñolo, M. Fajardo, R. Gil-Sanz, C. López-Mardomingo, P. Martin-Villa, A. Otero, M.M. Kubicki, Y. Mugnier, S. El Krami and Y. Mourad, Organometallics, 12 (1993) 381.
- [4] A. Antiñolo, F. Carrillo, M. Fajardo, S. García-Yuste and A. Otero, J. Organomet. Chem., 482 (1994) 93.
- [5] A. Antiñolo, M. Fajardo, S. García-Yuste, I. del Hierro, A. Otero, S. El Krami, Y. Mourad and Y. Mugnier, J. Chem. Soc., Dalton Trans., (1995) 3409.
- [6] A. Antiñolo, F. Carrillo-Hermosilla, M. Fajardo, S. García-Yuste, M. Lanfranchi, A. Otero, M.A. Pellinghelli, S. Prashar and E. Villaseñor, Organometallics, 15 (1996) 5507.
- [7] (a) A. Antiñolo, S. García-Lledó, J. Martínez de llarduya and A. Otero, J. Organomet. Chem., 335 (1987) 85; (b) A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. López-Mardomingo, A. Martín and A. Otero, J. Chem. Soc., Dalton Trans., (1995) 1007.

- [8] S. García-Yuste, unpublished results.
 [9] A. Antiñolo, M. Fajardo, F. Jalón, C. López-Mardomingo, A. Otero and C. Sanz-Bernabé, J. Organomet. Chem. 369 (1989) 187.
- [10] (a) J.F. Leboeuf, J.C. Leblanc and C. Moïse, J. Organomet. Chem., 335 (1987) 331: (b) G.E. Herberich and H. Mayer, J. Organomet. Chem., 322 (1987) C29: (c) V.C. Gibson and T.P. Kee, J. Organomet. Chem., 471 (1994)105.
- [11] E. Pretsch, T. Clerc, J. Seibl and W. Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Springer, Berlin, 1983
- [12] A. Antiñolo, unpublished results.
- [12] R. Hummon, and R.J. Phillips, Coord. Chem. Rev., 33 (1980) 227.
- [14] D. Lyons G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1984) 695.