Ethoxycarbonyl-, Cyano- and Methoxy-methyl Complexes of Nickel(II) and their Carbonylation Reactions†

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The oxidative addition of $ClCH_2CO_2Et$, $ClCH_2CN$ and $BrCH_2OMe$ to $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene), in the presence of 2 equivalents of PMe_3, affords the β-functionalized nickel(II) methyl derivatives *trans*-$[Ni(CH_2R)X(PMe_3)_2]$ (R = CO_2Et, X = Cl **1**; R = CN, X = Cl **2**; R = OMe, X = Br **3**). The interaction of these complexes with carbon monoxide has been studied. The methoxymethyl derivative **3** forms a stable acyl of composition *trans*-$[Ni\{C(O)CH_2OMe\}Br(PMe_3)_2]$ **7**, but for the ethoxycarbonylmethyl complex **1** the corresponding acyl **8** forms reversibly and, although stable as a solid, only exists in solution under an atmosphere of carbon monoxide. No stable acyl has been observed from the reaction of **2** with CO; only decomposition occurs. Stable 18-electron alkyl and acyl cyclopentadienyl derivatives of composition $[Ni(CH_2R)(\eta\text{-}C_5H_5)(PMe_3)]$ (R = CO_2Et **4**; CN **5**, or OMe **6**) and $[Ni\{C(O)CH_2R\}(\eta\text{-}C_5H_5)(PMe_3)]$ (R = OMe **9** or CO_2Et **10**) are easily obtained upon reaction of the above 16-electron complexes with $Na(C_5H_5)$. The new compounds have been fully characterized by analytical and spectroscopic (IR and ^1H, ^{13}C and ^{31}P NMR) methods.

Transition-metal alkyls of composition $L_nM{-}CH_2X$, in which the alkyl functionality contains carbon-based unsaturated groups [X = C(O)R, CO_2R, CN, $CH{=}CH_2$, *etc.*] or heteroatom substituents (X = halide, OR, SR, SiR_3, *etc.*) in the β position, have attracted considerable interest from organometallic chemists for many years.[1] This is partly due to the profound influence the presence of the β-substituent in the alkyl chain has on the bonding and reactivity properties of the M–C bond. Moreover, compounds of this type have found utility in various areas of fruitful research: generation of reactive carbene species,[2] $M{=}CH_2^+$, kinetic stabilization of transition metal-to-carbon bonds[3] (towards decomposition, hydrogen-elimination or CO insertion), aldol reactions[4,5] and others.[6,7]

Following recent studies by our group[8] on organometallic complexes of nickel stabilized by the small, strongly donating PMe_3 ligand, we now report the formation and carbonylation chemistry of some new 16- and 18-electron complexes of composition *trans*-$[Ni(CH_2R)X(PMe_3)_2]$ and $[Ni(CH_2R)(\eta\text{-}C_5H_5)(PMe_3)]$ which contain β-substituted alkyl chains. These include some ester enolates (R = CO_2Et) as well as some methoxy- and cyano-methyl derivatives (R = OMe and CN, respectively). The new compounds have been fully characterized by microanalysis, IR and multinuclear (^1H, ^{13}C and ^{31}P) NMR spectroscopies. While this work was in progress the synthesis and reactions of the first carbon-bound enolate derivatives of nickel were reported.[5]

Experimental

Microanalyses were by Pascher Microanalytical Laboratory, Remagen (Germany) and the Microanalytical Service of the University of Sevilla. Complexes **8** and **10** were not analysed owing to their instability and oily nature respectively; **4** and **6**, the cyclopentadienyl derivatives of **1** and **3**, for which analytical figures are available were only characterized by spectroscopy. The spectroscopic instruments used were Perkin-Elmer models 577 and 684 for IR spectra and Varian XL-200 for ^1H, ^{13}C and ^{31}P NMR spectra. The ^1H and ^{13}C resonances of the solvent were used as internal standards, but the chemical shifts are reported with respect to $SiMe_4$; ^{31}P NMR shifts are relative to external 85% H_3PO_4. All preparations and other operations were carried under oxygen-free nitrogen, following conventional Schlenk techniques. Solvents were dried and degassed before use. The light petroleum used had b.p. 40–60 °C. Trimethylphosphine was prepared by a literature method.[9]

The complex $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) was synthesised following the preparation reported by Colquhoun *et al.*[10] slightly modified as follows. To a stirred suspension of $[NiCl_2(py)_4]$ (py = pyridine) (59.5 g, 135 mmol) in tetrahydrofuran (thf) (100 cm^3) was added cycloocta-1,5-diene (50 cm^3, 400 mmol). Metallic sodium (6.2 g, 270 mmol) was cut into small pieces and added to the reaction mixture under a stream of nitrogen, with continuous stirring. Precipitation of a crystalline material $\{[Ni(cod)_2] + NaCl\}$ and darkening of the solution was observed (*ca.* 1 h). After stirring for 6 h the volatiles were removed under vacuum and MeOH added to induce complete crystallization of $[Ni(cod)_2]$. The mixture was filtered under N_2 through a sinter funnel which contained a bed of Celite, and the solid was washed with MeOH until the washing liquids became colourless. After drying the solid *in vacuo* the desired compound was extracted with several portions of hot toluene (90 °C) containing a small amount of cod (*ca.* 50:1 v/v). Upon cooling at −70 °C, $[Ni(cod)_2]$ (21.5 g, 59%) crystallized as yellow plates which were collected, washed thoroughly with cold (−30 °C) Et_2O and dried under vacuum.

$[Ni(CH_2CO_2Et)Cl(PMe_3)_2]$ **1**.—To a stirred suspension of $[Ni(cod)_2]$ (0.55 g, *ca.* 2 mmol) in diethyl ether (35 cm^3), cooled at −30 °C, were added PMe_3 (0.4 cm^3, 4 mmol) and $ClCH_2CO_2Et$ (0.21 cm^3, *ca.* 2 mmol). The reaction mixture was warmed to room temperature and stirred for 1 h, when a brown-orange solution was obtained. The solvent was removed under vacuum, the residue extracted with light petroleum (35 cm^3) and filtered to give a solution from which brown-orange crystals of the desired product **1** (0.50 g, *ca.* 75%) were collected after partial removal of the solvent and cooling overnight at −20 °C

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

(Found: C, 36.05; H, 7.60. $C_{10}H_{25}ClNiO_2P_2$ requires C, 36.00; H, 7.50%); $\nu_{max}(CO_2)/cm^{-1}$ 1660 (Nujol); $\delta_H(C_6D_6)$ 1.04 [3 H, t, $^3J(HH)$ 7.2, $CO_2CH_2CH_3$], 1.12 (18 H, br s, PMe_3), 1.25 (2 H, br s, $NiCH_2$) and 4.06 [2 H, q, $^3J(HH)$ 7.2 Hz, $CO_2CH_2CH_3$]; $\delta_C(C_6D_6)$ 1.0 (s, $NiCH_2$), 12.7 (br s, PMe_3), 14.6 (s, $CO_2CH_2CH_3$), 58.7 (s, $CO_2CH_2CH_3$) and 177.5 (s, CO_2Et); (−80 °C, thf–CD_3COCD_3) 1.2 [br t, $^2J(CP)$ 20, $NiCH_2$], 11.7 [t, $J(CP)_{app}$ 14 Hz, PMe_3], 15.1 (s, $CO_2CH_2CH_3$) and 58.9 (s, $CO_2CH_2CH_3$); $\delta_P(C_6D_6)$ −13.9 (s).

Reaction of $[Ni(CH_2CO_2Et)Cl(PMe_3)_2]$ *with* CO.—A thick-walled glass pressure reactor was filled with a solution of complex **1** (0.34 g, *ca.* 1 mmol) in light petroleum (20 cm^3) and pressurized with 4–5 atm of carbon monoxide. After *ca.* 10 min precipitation of a reddish microcrystalline solid was observed. The stirring was continued for 30 min, to complete precipitation of the product, when the solution became pale yellow. The solid was collected under an atmosphere of CO and dried under a stream of this gas. The IR spectrum of this material exhibited bands at 2000, 1735 and 1620 cm^{-1} (see Results and Discussion).

Pressurizing the reaction mixture with 2 instead of 4 atm of CO yielded, after *ca.* 15 min, a yellow microcrystalline product, *trans*-$[Ni\{C(O)CH_2CO_2Et\}Cl(PMe_3)_2]$ **8**, with IR bands at 1740 and 1620 cm^{-1}; $\delta_C(C_6D_6)$ 12.8 (br s, PMe_3), 14.3 (s, $CO_2CH_2CH_3$), 57.3 (s, $NiCOCH_2$) and 61.0 (s, $CO_2CH_2CH_3$); (−80 °C, thf–CD_3COCD_3) 11.9 [t, $J(CP)_{app}$ 14, PMe_3], 14.0 (s, $CO_2CH_2CH_3$), 57.6 (br s, $NiCOCH_2$), 60.9 (s, $CO_2CH_2CH_3$), 167.9 (s, CO_2Et) and 248.7 [t, $^2J(CP)$ 26 Hz, NiCOR]; $\delta_P(C_6D_6)$ −15.3 (s).

$[Ni(CH_2CO_2Et)(\eta\text{-}C_5H_5)(PMe_3)]$ **4**.—The complex $[Ni(CH_2CO_2Et)Cl(PMe_3)_2]$ (0.2 g, 0.6 mmol) was dissolved in thf (20 cm^3) and 1 equivalent of $Na(C_5H_5)$ (2 cm^3 of a 0.3 mol dm^{-3} solution in thf, 0.6 mmol) was added. The colour of the solution changed from brown-orange to green and, after 10 min of stirring, to dark red. After stirring for another hour the solvent was removed under vacuum and the residue extracted with light petroleum (30 cm^3). Partial removal of the solvent and cooling at −20 °C afforded 0.07 g of green crystals. Further concentration of the mother-liquor and cooling yielded a second crop of 0.03 g of compound **4** (0.1 g, 52%), $\nu_{max}(CO_2)/cm^{-1}$ 1675 (Nujol); $\delta_H(C_6D_6)$ 0.86 [9 H, d, $^2J(HP)$ 9.9, PMe_3], 1.10 [2 H, d, $^3J(HP)$ 8.2, $NiCH_2$], 1.12 [3 H, t, $^3J(HH)$ 7.2, $CO_2CH_2CH_3$], 4.08 [2 H, q, $^3J(HH)$ 7.2 Hz, $CO_2CH_2CH_3$] and 5.12 (5 H, s, C_5H_5); $\delta_C(C_6D_6)$ −13.1 [d, $^2J(CP)$ 19 Hz, $NiCH_2$], 14.7 (s, $CO_2CH_2CH_3$), 17.3 [d, $^1J(CP)$ 29 Hz, PMe_3], 58.0 (s, $CO_2CH_2CH_3$), 90.6 (s, C_5H_5) and 182.6 (s, CO_2Et); $\delta_P(C_6D_6)$ −2.6 (s).

Formation of $[Ni\{C(O)CH_2CO_2Et\}(\eta\text{-}C_5H_5)(PMe_3)]$ **10**.—Carbon monoxide was bubbled through a solution of complex **1** (0.24 g, 0.72 mmol) in thf (20 cm^3) with formation of a yellow-orange solution of complex **8**. Sodium cyclopentadienide was then added (2.4 cm^3 of a 0.3 mol dm^{-3} solution in thf). The colour of the mixture became red and after stirring for 1 h the solvent was stripped off, leaving a red oily residue which was extracted with light petroleum (30 cm^3). After centrifugation, partial removal of the solvent and cooling at −70 °C, red crystals of compound **10**, which melted upon warming at room temperature, were isolated (0.21 g, 75%), ν_{max}/cm^{-1} 1730 (CO), 1630 (CO); $\delta_H(C_6D_6)$ 0.85 [9 H, d, $^2J(HP)$ 9.8, PMe_3], 0.97 [3 H, t, $^3J(HH)$ 7.2, $CO_2CH_2CH_3$], 3.63 (2 H, s, $NiCOCH_2$), 3.97 [2 H, q, $^3J(HH)$ 7.2 Hz, $CO_2CH_2CH_3$] and 5.10 (5 H, s, C_5H_5); $\delta_C(C_6D_6)$ 14.0 (s, $CO_2CH_2CH_3$) 17.3 [d, $^1J(CP)$ 31, PMe_3], 59.9 (s, $CO_2CH_2CH_3$), 67.0 (s, $NiCOCH_2$), 89.9 (s, C_5H_5), 166.3 (s, CO_2Et) and 242.1 [d, $^2J(CP)$ 26 Hz, NiCOR]; $\delta_P(C_6D_6)$ −0.21 (s).

$[Ni(CH_2CN)Cl(PMe_3)_2]$ **2**.—To a cold (−60 °C) suspension of $[Ni(cod)_2]$ (0.84 g, 3 mmol) in Et_2O (40 cm^3) were successively added PMe_3 (0.6 cm^3, 6 mmol) and $ClCH_2CN$ (0.2 cm^3, *ca.* 3 mmol), *via* syringe, and the resulting mixture was stirred at room temperature for 5 h, to form an orange solution. Removal of the volatiles *in vacuo*, extraction with Et_2O–thf (10:20 cm^3) and cooling at −20 °C produced compound **2** as large orange-brown needles (0.43 g, 50%) (Found: C, 33.10; H, 7.10; N, 4.50. $C_8H_{20}ClNNiP_2$ requires C, 33.55; H, 7.00; N, 4.90%); $\nu_{max}(CN)/cm^{-1}$ 2190 (Nujol); $\delta_H(C_6D_6)$ 0.2 (2 H, br s, $NiCH_2$) and 0.9 (18 H, br s, PMe_3); $\delta_C(C_6D_6)$ −24.7 (s, $NiCH_2$), 12.1 (br s, PMe_3) and 124.4 (s, CN); $\delta_P(C_6D_6)$ −11.2(s).

Reaction of $[Ni(CH_2CN)Cl(PMe_3)_2]$ *with* CO.—Compound **2** (0.05 g) was dissolved in thf (10 cm^3) and through this solution a stream of CO was passed for 20 min, after which time the volatiles were removed *in vacuo*. From the resulting mixture, red $[NiCl_2(PMe_3)_2]$ was isolated and the IR spectrum of the residue indicated the presence of $[Ni(CO)_2(PMe_3)_2]$ and other by-products containing the C≡N functionality.

$[Ni(CH_2CN)(\eta\text{-}C_5H_5)(PMe_3)]$ **5**.—Complex **2** (0.27 g, 0.94 mmol) was dissolved in thf (30 cm^3) and the resulting solution cooled at −40 °C and treated with 1 equivalent of $Na(C_5H_5)$ (3.2 cm^3 of a 0.3 mol dm^{-3} solution in thf, 0.95 mmol) added *via* syringe. The mixture was stirred for 1 h at room temperature and then taken to dryness. The residue was extracted with a mixture of Et_2O (20 cm^3) and light petroleum (10 cm^3), and the resulting solution cooled at −70 °C. Green plates of compound **5** separated and were collected (0.18 g, 80%) (Found: C, 49.75; H, 6.85; N, 5.55. $C_{10}H_{16}NNiP$ requires C, 50.05; H, 6.65; N, 5.85%); $\nu_{max}(CN)/cm^{-1}$ 2185 (Nujol); $\delta_H(C_6D_6)$ 0.24 [2 H, d, $^3J(HP)$ 7.3, $NiCH_2$], 0.75 [9 H, d, $^2J(HP)$ 9.8, PMe_3] and 4.98 (5 H, s, C_5H_5); $\delta_C(C_6D_6)$ −40.2 [d, $^2J(CP)$ 22, $NiCH_2$], 16.6 [d, $^1J(CP)$ 29.1 Hz, PMe_3] and 90.8 (s, C_5H_5); $\delta_P(C_6D_6)$ −3.0 (s).

$[Ni(CH_2OMe)Br(PMe_3)_2]$ **3**.—The complex $[Ni(cod)_2]$ (0.82 g, 3 mmol) was stirred in Et_2O (50 cm^3) with PMe_3 (0.6 cm^3, 6 mmol). The mixture was then cooled at −50 °C and treated with a solution of $BrCH_2OMe$ (3 cm^3 of a 1 mol dm^{-3} solution in Et_2O, 3 mmol) to yield a suspension which was allowed to reach room temperature and then stirred for 3 h. The solvent was removed under reduced pressure and the residue extracted with light petroleum (50 cm^3); centrifugation, concentration of the resulting solution and cooling at −30 °C overnight furnished the desired product as large red-brown plates (0.62 g, 62%) (Found: C, 27.65; H, 6.75. $C_8H_{23}BrNiOP_2$ requires C, 28.50; H, 6.80%); $\delta_H(C_6D_6)$ 1.08 (18 H, br s, PMe_3), 3.37 (3 H, s, OCH_3) and 3.40 (2 H, s, $NiCH_2$); $\delta_C(C_6D_6)$ 13.5 [d, $J(CP)_{app}$ 23 Hz, PMe_3], 60.7 (s, OCH_3) and 62.7 (s, $NiCH_2$); $\delta_P(C_6D_6)$ −14.1 (s).

Reaction of $[Ni(CH_2OMe)Br(PMe_3)_2]$ *with Carbon Monoxide*.—Carbon monoxide was bubbled at room temperature and pressure through a solution of compound **3** (0.15 g, *ca.* 0.45 mmol) in diethyl ether (20 cm^3) for 20 min. The solution became orange and was evaporated to dryness. The residue was dissolved in Et_2O (30 cm^3) and centrifuged to remove a small amount of an insoluble material. After concentration, addition of light petroleum (5 cm^3) and cooling overnight, the compound $[Ni\{C(O)CH_2OMe\}Br(PMe_3)_2]$ **7** was obtained as yellow-brown crystals (0.11 g, 73%) (Found: C, 29.45; H, 6.40. $C_9H_{23}BrNiO_2P_2$ requires C, 29.70; H, 6.85%); $\nu_{max}(CO)/cm^{-1}$ 1640 (Nujol); $\delta_H(CD_3COCD_3)$ 1.30 (18 H, br s, PMe_3), 3.54 [2 H, s, $NiC(O)CH_2$] and 3.72 (3 H, s, OCH_3); $\delta_C(CD_3COCD_3)$ 14.0 (br s, PMe_3), 59.7 (s, OCH_3) and 83.6 [s, $NiC(O)CH_2$]; $\delta_P(CD_3COCD_3)$ −10.5 (s).

$[Ni(CH_2OMe)(\eta\text{-}C_5H_5)(PMe_3)]$ **6**.—To a stirred solution of complex **3** (0.66 g, 2 mmol) in Et_2O (20 cm^3) was added an excess of $Na(C_5H_5)$ (3 cm^3 of a 1 mol dm^{-3} solution in thf). Precipitation of a solid and formation of a reddish solution was observed. The mixture was stirred for 2 h and the solvent eliminated under reduced pressure. The residue was extracted with light petroleum and the resulting solution concentrated and cooled at −70 °C. Red crystals of the expected product were formed. The supernatant liquid was decanted and the crystals dried under vacuum at low temperature. The compound was recrystallized following the above procedure and when allowed to reach room temperature melted forming a red oil which was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopies as the complex $[Ni(CH_2OMe)(\eta\text{-}C_5H_5)(PMe_3)]$ **6** (0.29 g, 60%); $\delta_H(C_6D_6)$ 0.85 [9 H, d, ^2J(HP) 9.4, PMe_3], 3.20 (3 H, s, OCH_3), 4.23 [2 H, d, ^3J(HP) 5.0 Hz, $NiCH_2$] and 5.16 (5 H, s, C_5H_5); $\delta_C(C_6D_6)$ 17.6 [d, ^1J(CP) 28, PMe_3], 53.2 [d, ^2J(CP) 25 Hz, $NiCH_2$], 59.1 (s, CH_3) and 89.5 (s, C_5H_5); $\delta_P(C_6D_6)$ 1.7 (s).

$[Ni\{C(O)CH_2OMe\}(\eta\text{-}C_5H_5)(PMe_3)]$ **9**.—To a solution of complex **7** (0.11 g, 0.4 mmol) in thf (15 cm^3) was added $Na(C_5H_5)$ (0.6 cm^3 of a 0.55 mol dm^{-3} solution in thf) at room temperature. After stirring for 1 h and removing the solvent at reduced pressure, the desired compound **9** was obtained as red crystals from light petroleum solutions (0.08 g, 88%) (Found: C, 48.55; H, 7.10. $C_{11}H_{19}NiO_2P$ requires C, 48.40; H, 7.00%); ν_{max}(CO)/cm^{-1} 1630 (Nujol); $\delta_H(C_6D_6)$ 0.75 [9 H, d, ^2J(HP) 9.6 Hz, PMe_3], 3.32 (3 H, s, OCH_3), 3.90 [2 H, s, $NiC(O)CH_2$] and 5.14 (5 H, s, C_5H_5); $\delta_C(C_6D_6)$ 17.2 [d, ^1J(CP) 30, PMe_3], 59.0 (s, OCH_3), 87.9 [s, $NiC(O)CH_2$], 89.3 (s, C_5H_5) and 250.3 [d, ^2J(CP) 23 Hz, NiCOR]; $\delta_P(C_6D_6)$ 0.0 (s).

Results and Discussion

Several methods can be used for the preparation of transition metal enolates,[5] among them: (*i*) reaction of a metal anion with an α-halogeno (or related) carbonyl compound; (*ii*) interaction of a metal halide complex with a main-group enolate; and (*iii*) action of an enol silane on a metal chloride or metal alkoxide. A relatively large number of nickel(II) compounds containing Ni–C bonds can however be prepared by the oxidative addition of organic halides to appropriate nickel(0) precursors, in the presence of suitable stabilizing ligands,[11] and this approach can be successfully used for the synthesis of the nickel-ester enolate *trans*-$[Ni(CH_2CO_2Et)Cl(PMe_3)_2]$ **1**, and of the cyano- and methoxy-methyl complexes analogues *trans*-$[Ni(CH_2R)X(PMe_3)_2]$ (R = CN, X = Cl **2**; R = OMe, X = Br **3**).

Several nickel(0) compounds, including $[Ni(PMe_3)_4]$, can in principle be employed as starting materials. The best results are, however, obtained using the readily available $[Ni(cod)_2]$ which reacts with $ClCH_2CO_2Et$, in the presence of 2 equivalents of PMe_3, to provide high yields of the desired ethoxycarbonylmethyl complex **1** [equation (1)]. The carbon-bound structure proposed for **1** is assigned on the basis of the infrared and ^{1}H and ^{13}C NMR data (see Experimental section). Thus, a medium-intensity absorption at *ca.* 1660 cm^{-1} can be attributed to ν(CO) of the ester functionality. The energy of this band may seem rather low for an ester group (there is a shift of *ca.* 80 cm^{-1} to lower wavenumber with respect to an appropriate reference such as $MeCO_2Et$) but it is within the range 1720–1660 cm^{-1} found for this kind of carbon-bound enolate.[4,5,12–18] The lowering of this band has been sometimes attributed to the so-called 'β effect'.[4,18] The observation of a triplet at *ca.* δ 1.2 [^2J(CP) 20 Hz] in the ^{13}C-{^{1}H} NMR spectrum of **1** recorded at −80 °C supports the proposed formulation and it is in agreement with a *cis* distribution of the ethoxycarbonylmethyl group with respect to the two equivalent *trans* phosphine ligands.

$$[Ni(cod)_2] + ClCH_2CO_2Et + 2PMe_3 \longrightarrow \underset{\mathbf{1}}{trans\text{-}[Ni(CH_2CO_2Et)Cl(PMe_3)_2]} \quad (1)$$

Complex **1** is a fluxional molecule in solution, the methyl groups of the phosphine ligands yielding at room temperature broad singlets both in the ^{1}H and in the ^{13}C-{^{1}H} NMR spectra. This evidences the existence of an interchange process involving the PMe_3 ligands. Under these conditions, the nickel-bound methylene group gives rise to broad ^{1}H and ^{13}C-{^{1}H} singlets, showing that the exchange process is intermolecular. The observed changes are probably due to traces of PMe_3 present in solution which readily form transient, five-co-ordinate, tris(phosphine) species.[19] The ester group is characterized by a ^{13}C resonance at δ 178, again very close to the values normally found for this type of complex (around δ 180, see for example refs. 16–18).

As already mentioned, the cyano- and methoxy-methyl complexes, *trans*-$[Ni(CH_2R)X(PMe_3)_2]$ **2** and **3**, can be prepared following an essentially identical procedure. Both are highly crystalline solids, unstable towards moisture and oxygen in solution and in the solid state. The cyanomethyl derivative[18] **2** displays an infrared absorption at 2190 cm^{-1} due to ν(C≡N) while for the methoxymethyl complex **3** no characteristic IR bands are observed,[15,17,20] with the exception of a strong absorption at *ca.* 950 cm^{-1} associated with the co-ordinated PMe_3 ligands. The most significant spectroscopic feature of these compounds is the observation of a strong opposite substituent effect on the ^{13}C NMR resonance (δ −25 and 61 for **2** and **3**, respectively) corresponding to the nickel-bonded methylene group.[17]

Carbon-bound nickel enolates of composition $[Ni\{CHR^1C(O)R^2\}L(PPh_3)]$ (L = C_5H_5 or C_5Me_5; R^1 = H or Me; R^2 = Bu^t, Ph or OBu^t) have recently been prepared by Bergman and co-workers[5] by halide displacement from the metal complexes, $[NiCl(L)(PPh_3)]$, by the appropriate main-group enolate. A related compound, $[Ni(CH_2CO_2Et)(\eta\text{-}C_5H_5)(PMe_3)]$ **4**, can be obtained as a green crystalline material following the reaction of **1** with $Na(C_5H_5)$ in tetrahydrofuran [equation (2)]. Complex **4** is a rigid molecule in solution for which spectroscopic data are fully in accord with the proposed formulation: ν_{max}(CO)/cm^{-1} 1675; ^{13}C-{^{1}H} resonances at δ 183 (s) and −13 [d, ^2J(CP) 19 Hz] for the carboxy and the nickel-bound methylene carbons, respectively. The analogous reactions of $Na(C_5H_5)$ with compounds **2** and **3** furnishes the related species $[Ni(CH_2R)(\eta\text{-}C_5H_5)(PMe_3)]$ (R = CN **5** or OMe **6**). Relevant spectroscopic data for **5** and **6** are provided in the Experimental section and need no further comment.

$$\underset{\mathbf{1}}{trans\text{-}[Ni(CH_2CO_2Et)Cl(PMe_3)_2]} + Na(C_5H_5) \xrightarrow[-PMe_3]{thf} \underset{\mathbf{4}}{[Ni(CH_2CO_2Et)(\eta\text{-}C_5H_5)(PMe_3)]} + NaCl \quad (2)$$

The insertion of CO into transition metal-carbon bonds is a fundamental process in organometallic chemistry, both in stoichiometric and in catalytic transformations.[21] Since, on the other hand, carbonylations involving M–CH_2OR and M–CH_2CO_2R moieties can be used as models for the preparation of organic products from synthesis gas,[6] one of the main objectives of the present work was the study of the reaction of CO with the β-functionalized alkyl derivatives described above.

It is known that the presence of polar, electronegative substituents in the α position of the alkyl chain increases the kinetic stability of the M–C bond towards insertion.[3,22] In spite of this fact, several successful direct carbonylations (CO as the reagent) have been reported for M–CH_2OR systems.[15,17,20] For the alkoxycarbonylmethyl derivatives, however, this process is considerably more difficult[17,23] and effectively to promote the carbonylation reaction the presence of an oxidizing agent,[24] or of an additional ligand,[17] is needed. The resulting M–$C(O)CH_2CO_2R$ products are usually unstable to decarbonylation.

Action of CO (20 °C, 1 atm) upon solutions of the methoxymethyl complex **3** affords high yields of the stable (towards decarbonylation) acyl *trans*-$[Ni\{C(O)CH_2OMe\}Br$-

$(PMe_3)_2]$ **7** [equation (3)]. The nickel–acyl linkage yields a

$$\underset{\mathbf{3}}{trans\text{-}[Ni(CH_2OMe)Br(PMe_3)_2]} \xrightarrow{CO} \underset{\mathbf{7}}{trans\text{-}[Ni\{C(O)CH_2OMe\}Br(PMe_3)_2]} \quad (3)$$

medium-intensity IR absorption at 1640 cm^{-1}, *i.e.* in the region expected for nickel acyls.[25] The NMR data (see Experimental section) are also in accord with the proposed formulation. Contrary to **3**, the reaction of the cyanomethyl derivative **2** with CO does not furnish the expected acyl. Instead, a disproportionation process, giving $[NiCl_2(PMe_3)_2]$ and $[Ni(CO)_2(PMe_3)_2]$ among other unidentified products, takes place.

A rather complex, albeit interesting, behaviour is exhibited by the ethoxycarbonylmethyl derivative **1**. When light petroleum solutions of this complex are pressurized with 2 atm of CO a yellow microcrystalline solid $[Ni\{C(O)CH_2CO_2Et\}Cl(PMe_3)_2]$ **8** precipitates slowly. This material shows characteristic IR bands at 1740 and 1620 cm^{-1}, respectively attributed to the ester and acyl functionalities. When this complex is dissolved in common organic solvents under an atmosphere of N_2, CO is quickly released and the starting alkyl **1** is reformed. Thus, the carbonylation process can be represented by means of the equilibrium (4). In solution, and under carbon monoxide,

$$\underset{\mathbf{1}}{trans\text{-}[Ni(CH_2CO_2Et)Cl(PMe_3)_2]} \xrightleftharpoons[-CO]{+CO} \underset{\mathbf{8}}{trans\text{-}[Ni\{C(O)CH_2CO_2Et\}Cl(PMe_3)_2]} \quad (4)$$

this equilibrium is totally shifted to the right-hand side, but in the absence of this gas only the parent alkyl **1** is detected at room temperature. The stability of complex **8** towards deinsertion when kept under an atmosphere of CO allows its full spectroscopic characterization. As already mentioned, the ester moiety yields an IR absorption at 1740 cm^{-1}. This is *ca.* 80 cm^{-1} higher than for the parent alkyl **1**, indicating the disappearance of the β effect upon insertion. Similarly, the ^{13}C resonance of the carboxylic carbon appears now at δ 168 (δ 178 for **1**). Both these values are in accord with literature data for the few reported complexes of this kind[16,17,26] and suggest in addition the absence of interaction between the metal centre and the CO_2R carbonyl group, contrary to what has been proposed for a related iridium complex.[14] Finally, the acyl carbon is characterized by a low-field triplet [δ 249, $^2J(CP)$ 26 Hz] in the $^{13}C\text{-}\{^1H\}$ NMR spectrum recorded at −80 °C. Acyl **8** exhibits a fluxional behaviour analogous to that described above for the parent alkyl.

It is worth mentioning at this point that when the reaction of complex **1** with CO is carried out at higher pressures (4–5 atm) a brick-red precipitate is obtained instead. This has IR bands at 2000, 1735 and 1620 cm^{-1}, which can be respectively attributed to ν(C–O) of a terminal carbonyl ligand, an ester and an acyl functionality. The complex is unstable, slowly decomposing in solution even when kept under CO. As a solid it is stable under CO but it releases this gas under vacuum, as shown by the decrease in intensity of the band of 2000 cm^{-1}. Although the instability of this compound precludes its full spectroscopic characterization, on the basis of the available data it can be formulated as the five-co-ordinate, 18-electron carbonyl adduct $[Ni\{C(O)CH_2CO_2Et\}Cl(CO)(PMe_3)_2]$. A somewhat related carbonyl complex of Ni^{II} has been characterized by X-ray crystallography.[27]

As described above, compounds **1** and **3** react cleanly and fastly with CO to afford the corresponding acyls, of which $[Ni\{C(O)CH_2CO_2Et\}Cl(PMe_3)_2]$ is the less stable towards decarbonylation. Since reactions of this type are usually reversible in 16-electron nickel(II) systems[25] the observed stability must be thermodynamic in nature, and this is in agreement with literature precedents which, as already commented, demonstrate that $M\text{–}CH_2CO_2R$ species are difficult to carbonylate.[17] Complex **8** constitutes the first example of an isolable species obtained by direct carbonylation of a well characterized $M\text{–}CH_2CO_2R$ compound. The $Ni\text{–}C(O)CH_2CO_2Et$ functionality can, however, be kinetically stabilized by substitution of the Cl and one of the PMe_3 ligands by a cyclopentadienyl group. This is discussed below.

Although the 18-electron cyclopentadienyl derivatives **4**–**6** do not react with CO under the above conditions, the corresponding acyls $[Ni\{C(O)CH_2R\}(\eta\text{-}C_5H_5)(PMe_3)]$ (R = OMe **9** or CO_2Et **10**) can be obtained by the indirect route shown in equation (5). Compounds **9** and **10** are red crystalline

$$\underset{\mathbf{7,8}}{trans\text{-}[Ni\{C(O)CH_2R\}X(PMe_3)_2]} \xrightarrow[-NaX,\ -PMe_3]{Na(C_5H_5)} [Ni\{C(O)CH_2R\}(\eta\text{-}C_5H_5)(PMe_3)] \quad (5)$$
$$R = OMe\ \mathbf{9}\ \text{or}\ CO_2Et\ \mathbf{10}$$

solids, which display a ^{13}C resonance at δ 240–250 [doublet, $^2J(CP)$ *ca.* 23 Hz] and an IR absorption at *ca.* 1630 cm^{-1}, associated with the nickel-σ-acyl linkage. They are stable against decarbonylation to the parent alkyls and while for **9** this is probably a reflection of its thermodynamic stability, for **10**, in light of the above considerations regarding the formation of **8** and its decarbonylation to **1**, the observed stability must be largely kinetic in origin. Other reported stable compounds of this type are $[Rh\{C(O)CH_2CO_2Et\}(\eta\text{-}C_5H_5)Br(PPh_3)]$[26] and $[Fe\{C(O)CH_2CO_2Et\}(CO)_2(NO)(PPh_3)]$,[28] both obtained by oxidative addition of XCH_2CO_2Et to appropriate low-valent carbonyl substrates. While the first may be kinetically stabilized, as proposed for compound **10**, the situation is less clear for the iron compound which, in light of the above arguments, may require reformulation as an alkyl complex containing a $Fe\text{–}CH_2CO_2Et$ functionality.

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