New Nickel–Carbon Dioxide Complex: Synthesis, Properties, and Crystallographic Characterization of (Carbon dioxide)-bis(tricyclohexylphosphine)nickel

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Summary $[Ni(CO_2)(PCy_3)_2]$,0·75(C_7H_8), where Cy = cyclohexyl, can be made either by treating $[Ni(PCy_3)_3]$ or $[\{Ni(PCy_3)_2\}_2N_2]$ with CO_2 in toluene, or by direct reduction of $[NiBr_2(PCy_3)_2]$ with sodium sand under CO_2; the complex is planar, the CO_2 ligand possesses bent geometry and is co-ordinated through the carbon atom and one of the oxygen atoms.

Several transition metal complexes able to co-ordinate CO_2[1] or to act as catalysts in CO_2 fixation[2] have been described recently. Extending previous studies on Ni^I and Ni^0 complexes with tertiary phosphines,[3] we have investigated the direct reduction of $[NiX_2L_2]$ complexes [X = Cl, Br; L = PCy_3, PBu^n_3, PEt_2Ph,PEt_3; Cy = cyclohexyl] with sodium under CO_2, and the reaction of NiL_4 (L = PBu^n_3,PEt_2Ph, PEt_3), $[Ni(PCy_3)_3]$, and $[\{Ni(PCy_3)_2\}_2N_2]$ and CO_2. The stability of the carbon dioxide complexes is related to the basicity of the phosphines. We report the preparation, properties, and structure of $[Ni(CO_2)(PCy_3)_2]$, 0·75 toluene.

Treatment of $[Ni(PCy_3)_3]$ or $[\{Ni(PCy_3)_2\}_2N_2]$ with CO_2 in toluene at room temperature affords red-orange crystals which are air-stable for a few hours, and analysing for $[Ni(CO_2)(PCy_3)_2]$,0·75toluene (I). Reduction of $[NiBr_2(PCy_3)_2]$ with sodium sand in toluene under CO_2 gives (I) which is converted into $[Ni(CO)_2(PCy_3)_2]$ (II) and other products at longer reaction times.

The i.r. spectrum of (I) shows bands at 1740(vs), 1698(vw), and 1150(s) cm^{-1} (Nujol mull). These bands are assigned to the co-ordinated carbon dioxide acting as a bidentate ligand. The reflectance spectrum of (I) in MgO shows maxima at 270 and 350 nm, with a broad shoulder at 440 nm.

When (I) is treated with triphenyl phosphite at room temperature, CO_2 is evolved quantitatively, and if argon is bubbled through a solution of (I) in toluene at room temperature, CO_2 is released in the ratio CO_2:Ni, 1 : 1, (shown by gas chromatography) supporting the presence of CO_2 as a ligand. The starting material can be recovered when the resulting solution is exposed to CO_2.

The molecular structure of (I) has been unambiguously established by a single crystal study. The complex crystallizes in the triclinic space group $P\bar{1}$ with a = 19·03(2), b = 12·18(1), c = 9·64(1) Å, α = 96·3(1), β = 100·2(1),

$\gamma = 99{\cdot}1(1)$, $D_m = 1{\cdot}19(2)$, $D_c = 1{\cdot}13\ \mathrm{g\ cm^{-3}}$, $Z = 2$. A Fourier map obtained from 2448 diffraction data collected by counter methods has shown that the complex is monomeric and the co-ordination about the metal atom is planar; $R = 0{\cdot}11$. The CO_2 molecule is markedly bent and is co-ordinated through the carbon and one of the oxygen atoms (Figure). This is the first structural report of the co-ordinated CO_2 molecule; the mode of bonding of CO_2 is very similar to that of CS_2 in $[Pt(CS_2)(PPh_3)_2]$.[4]

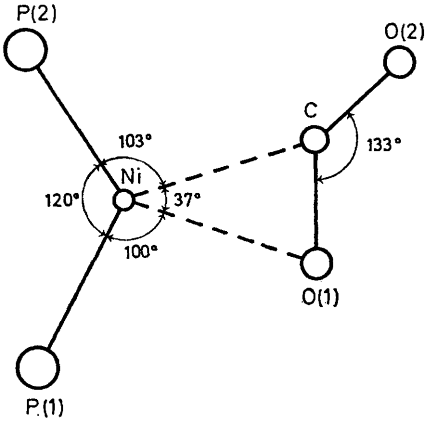

Figure. Mode of bonding of CO_2 in $[Ni(CO_2)(PCy_3)_2],0{\cdot}75$-toluene. Ni–C 1·84, Ni–O(1) 1·99, C–O(1) 1·22, C–O(2) 1·17 Å, e.s.d. 0·02 Å.

Comparison of the bond lengths in the Figure with those in free CO_2 (1·16 Å) shows that only the bond distance between the atoms co-ordinated to the metal is significantly altered.

Compound (I) in light petroleum releases CO_2 (in a CO_2 atmosphere) and is converted into yellow crystals analysing for $[\{Ni(PCy_3)_2\}_2(CO_2)]$ (III) [ν 1742(sh), 1736(vs), 1695 (vw), and 1148(s) cm^{-1}], which could be the complex described by Jolly and his co-workers.[1a] Solid $[Ni(PCy_3)_2]$ and $[\{Ni(PCy_3)_2\}_2N_2]$ treated with CO_2 (gas, 1 atm) at room temperature give $[Ni(CO_2)(PCy_3)_2]$ (IV) as a yellow-orange powder [ν 1728(vs), 1685(vw), and 1172(s) cm^{-1}]. Crystallization of (IV) from toluene affords (I).

Heating of solid (I) at 83 °C (under argon) affords a mixture of products (A) from which $[Ni(CO)_2(PCy_3)_2]$ has been isolated pure [ν (Nujol mull) 1982(vs) and 1920(vs) cm^{-1}; ν (toluene) 1980(vs) and 1912(s) cm^{-1}, agreeing with the values of Tolman[5]]. Phosphine oxide was not detected, but the presence of carbonate species and oxidation products from toluene of crystallization can be inferred from spectroscopic evidence. The same trend is observed when (I) is heated at 80 °C in toluene under CO_2, or when solid samples are gradually heated to 240 °C *in vacuo* or under argon. Conversely, rapid heating of solid (I) to 240 °C under argon affords CO_2 ($>$ 90%) and small amounts of carbonyl and carbonate species.

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