(Carbon dioxide)bis(trialkylphosphine)nickel Complexes

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The reaction of $[NiL_4]$ (L = PEt_3 or $PBu^n{}_3$) with CO_2 in toluene affords complexes of formula $[Ni(CO_2)L_2]$, *via* the $[Ni(CO_2)L_3]$ species. The reaction of $[Ni(CO_2)\{P(C_6H_{11})_3\}_2]\cdot0.75C_6H_5Me$ with O_2 to give (peroxocarbonato)-bis(tricyclohexylphosphine)nickel(II) is also reported.

WE recently reported[1] the structure and properties of $[Ni(CO_2)\{P(C_6H_{11})_3\}_2]\cdot0.75C_6H_5Me$ (1). As an extension of our studies we have investigated the reaction of $[NiL_4]$ ($L = PR_nPh_{3-n}$, R = alkyl, n = 1—3) with CO_2 and the reaction of the carbon dioxide complexes with O_2 and other agents. We report here the preparation and properties of $[Ni(CO_2)(PEt_3)_2]$ (2), $[Ni(CO_2)(PBu^n{}_3)_2]$ (3), and $[Ni(CO_4)\{P(C_6H_{11})_3\}_2]$ (4).

RESULTS AND DISCUSSION

Exposure of the violet solution[2] of $[Ni(PEt_3)_4]$ in toluene to 1 atm † of CO_2 at room temperature produced little change in colour, while the i.r. spectrum showed a medium band at 1 750 cm^{-1} with a shoulder at 1 735 cm^{-1}, attributable to ν(C=O) of co-ordinated CO_2. On cooling the CO_2-saturated solution to —30 °C, the colour changed to light orange and yellow crystals were deposited which analysed for $[Ni(CO_2)(PEt_3)_2]$ (2). Similarly, the red solution of $[Ni(PBu^n{}_3)_4]$ in toluene, when saturated with CO_2, showed in its i.r. spectrum a band at 1 760 cm^{-1} with a shoulder at 1 742 cm^{-1}. On cooling to —70 °C the colour changed to pale orange and pale yellow crystals of $[Ni(CO_2)(PBu^n{}_3)_2]$ (3) precipitated.

Both (2) and (3) are moderately stable to the air in the solid state and lose 1 mol of CO_2 per Ni atom when treated with iodine (or sulphuric acid) in benzene at room temperature. Heating of the complexes *in vacuo* results in variable amounts of CO_2 and causes decomposition of the phosphines.

The i.r. spectra of solid (2) and (3) (Nujol mulls) gave bands of co-ordinated CO_2, assigned as in the Table. These values are diagnostic of both a reduced bond order and of a lower symmetry for the co-ordinated CO_2. The Ni–CO_2 bond can be described by a molecular wavefunction comprised of charge-transfer and excited-state wavefunctions of the metal moiety and CO_2.[3] Although

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† Throughout this paper: 1 atm = 101 325 Pa; 1 eV ≈ 1.60 × 10^{-19} J; 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassero, *J.C.S. Chem. Comm.*, 1975, 636.

[2] M. Aresta, C. F. Nobile, and A. Sacco, *Inorg. Chim. Acta*, 1975, **12**, 167.

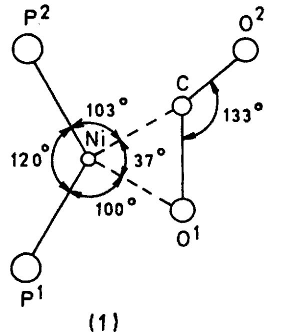
[3] M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassero, unpublished work.

the ν_{asym}(C=O) values for the complexes (2) and (3) (1 660 cm^{-1}) are close to that reported by Hartman and Hisatsune[4] for the antisymmetric stretching frequency of CO_2^- (1 671 cm^{-1}), allowing for the low oxidation state of the Ni atom, we assume that the contribution of the neutral excited states * is larger than that of the ionic functions, in agreement with the conclusions of Mason and Rae[6] on the complex $[Pt(CS_2)(PPh_3)_2]$. A Walsh diagram[7] for CO_2 shows that the energy of the unoccupied doubly degenerate $2\pi_u$ CO_2 molecular orbital decreases by 2 eV in going from the linear to the bent (130°) conformation, making these orbitals suitable for π bonding. From the ν(C=O) stretching frequencies it can be inferred that the Ni–CO_2 interaction in (2) and (3) is somewhat stronger than in (1). On the basis of the basicity,[8] nucleophilicity,[9] and steric hindrance[10] of the phosphines used [$P(C_6H_{11})_3$, pK_a 9.70, log k_2 −2.68,† cone angle 179 ± 10°; PEt_3, pK_a 8.69, log k_2 −2.81, cone angle 132 ± 4°; PBu^n_3, pK_a 8.43, log k_2 −2.79, cone angle 130 ± 4°], we propose that in the present case the major influence is that of the steric effect on the co-ordination symmetry around the metal. Also, the strength of the Ni–CO_2 bond should decrease on increasing the acidity of the phosphorus ligand.

Infrared bands (cm^{-1}) for co-ordinated CO_2 (Nujol mull)

Complex	ν(C=O)	ν_{asym}(CO)	ν_{sym}(CO)	π	Ring deformation	ν(O–O–)	δ(OCO)
$[Ni(CO_2)\{P(C_6H_{11})_3\}_2]\cdot 0.75C_6H_5Me$ (1) [a]	1 740br, vs 1 698w	1 150vs	1 094ms [b]	845s	730m [b]		
$[Ni(CO_2)(PEt_3)_2]$ (2)	1 660vs, 1 635vs	1 203vs	1 009s	828s	750s [c]		
$[Ni(CO_2)(PBu^n_3)_2]$ (3)	1 660vs, 1 632vs	1 200vs	1 008s	825s	750s		
$[Ni(CO_4)\{P(C_6H_{11})_3\}_2]$ (4)	1 625s, br [d]	1 162s		858m	750m	760	573, 553

[a] See ref. 1. [b] Tentatively assigned. $P(C_6H_{11})_3$ and $[NiX_2L_2]$, $[\{NiXL_2\}_2]$, $[NiL_3]$, and $[(NiL_2)_2N_2]$ absorb in this range. [c] The complex shows bands at 777s and 752vs cm^{-1}. The assignment is uncertain as $[NiBr_2L_2]$ and $[NiL_4]$ show bands almost in the same range. [d] This band can be resolved into two bands centred at 1 632 and 1 618 cm^{-1}.



(1)

1,2-Bis(diphenylphosphino)ethane (dppe) did not give isolable complexes of formula [Ni(CO_2)(dppe)]. This can be explained by taking in account both the nature of the Ni–CO_2 bond and the chelating ability of dppe. Bearing in mind the distorted square-planar geometry of (1), the substitution of the two $P(C_6H_{11})_3$ ligands by dppe can cause the P^1–Ni–P^2 bond angle to become less than 120°,‡ and the P^1–Ni–C bond angle to approach 180 °C, so that the *trans*-bond-weakening effect of P^1 of the dppe ligand on the Ni–C bond could reduce the strength of the Ni–CO_2 interaction.

I.r., U.v., and Visible Spectra.—As reported above the i.r. spectra of the toluene solutions of (2) and (3) show ν(C=O) shifted by 90 and 100 cm^{-1} towards higher wavenumbers with respect to the solid samples. Such a difference cannot be explained only on the basis of solvent effects. In fact $[Ni(CO_2)\{P(C_6H_{11})_3\}_2]$ shows a shift of only 12 cm^{-1} between the solid state and solution (1 728 and 1 740 cm^{-1}, respectively). We explain these results (and the changes in colour of the solutions) on the basis of equations (1)—(3). We attribute the i.r. bands

$$\underset{\text{colourless}}{[\mathrm{NiL_4}]} \xrightleftharpoons{\text{toluene}} \underset{\text{red or violet}}{[\mathrm{NiL_3}]} + \mathrm{L} \qquad (1)$$

$$[\mathrm{NiL_3}] + \mathrm{CO_2} \xrightleftharpoons{\text{toluene}} \underset{\text{light orange}}{[\mathrm{Ni(CO)_2L_3}]} \qquad (2)$$

$$[\mathrm{Ni(CO_2)L_3}] \xrightleftharpoons[\text{room temperature}]{\text{toluene, low temperature}} \underset{\text{yellow}}{[\mathrm{Ni(CO_2)L_2}]} + \mathrm{L} \qquad (3)$$

at 1 750 and 1 760 cm^{-1} respectively to $[Ni(CO_2)(PEt_3)_3]$ and $[Ni(CO_2)(PBu^n_3)_3]$. That this is correct is demonstrated by the fact that addition of PEt_3 to a saturated solution of $[Ni(CO_2)(PEt_3)_2]$ in toluene enhanced the solubility § of the complex and the i.r. spectrum of the solution showed bands at 1 750 and 1 735 (sh) cm^{-1} besides weak bands at 1 680 and 1 650 cm^{-1} which we assign to the unchanged $[Ni(CO_2)L_2]$ species, with a shift

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* It is worth noting that in (1) the O–C–O bond angle is 133°, very close to that calculated for the $^2A_1$ excited state of CO_2 (137°).[5]

† k_2 is the rate constant for the S_N2 reaction of the phosphines with EtI.

‡ The P^1–M–P^2 bond angle in complexes containing chelated dppe ranges from 85 to 90° (*e.g.* ref. 11).

§ Once isolated from the toluene solution the complexes $[Ni(CO_2)L_2]$ are only sparingly soluble in toluene or benzene.

[4] K. O. Hartman and I. C. Hisatsune, *J. Chem. Phys.*, 1966, **44**, 1913.

[5] C. R. Claydon, G. A. Segal, and H. S. Taylor, *J. Chem. Phys.*, 1970, **52**, 3387.

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[7] J. W. Rabalais, J. M. McDonald, V. Scerr, and S. P. McGlynn, *Chem. Rev.*, 1971, **71**, 73.

[8] Wm. A. Henderson, jun., and C. A. Streuli, *J. Amer. Chem. Soc.*, 1960, **82**, 5791.

[9] Wm. A. Henderson, jun., and S. A. Buckler, *J. Amer. Chem. Soc.*, 1960, **82**, 5794.

[10] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[11] U. G. Gregory, S. D. Ibekwe, B. T. Kilbourne, and D. R. Russel, *J. Chem. Soc. (A)*, 1971, 1118.

of *ca.* 20 cm^{-1} towards higher wavenumbers with respect to the solid sample owing to the solvent effect.

Further support comes from analysis of the u.v. spectra (Figure 1). The strong band at 505 nm (under argon) is assigned to the $[NiL_3]$ species formed on dissociation of the $[NiL_4]$ complexes in solution[2,12,13] [stage (1)]. Exposure of this solution to CO_2 resulted in fading of the colour and decrease of the intensity of the band associated with the three-co-ordinate species which is converted into four-co-ordinate $[Ni(CO_2)L_3]$ [stage (2)]. This behaviour is characteristic of the change in co-ordination number from three to four for nickel(0) complexes.[2,12,13] It is worth noting that exposure of $[NiL_4]$ solutions to an N_2 atmosphere produces an identical change in the u.v. spectrum as a consequence of the formation of the $[Ni(N_2)L_3]$ species (L = PEt_3,[2,13] $PBu^n{}_3$,[2] or PEt_2Ph [2]). The adducts $[Ni(CO_2)L_3]$ can be tentatively described as four-co-ordinate nickel(0) complexes with distorted planar geometry, where the CO_2 is bonded to the metal through the carbon atom.

We also find that equilibria (1)—(3) are sensitive to the concentrations of L and CO_2 in the solutions. When working with concentrated solutions of $[NiL_4]$ in toluene, on cooling, the only products isolated were the starting complexes. With dilute solutions, $[Ni(CO_2)L_2]$ could be isolated, equilibria (1) and (3) being shifted to the right.

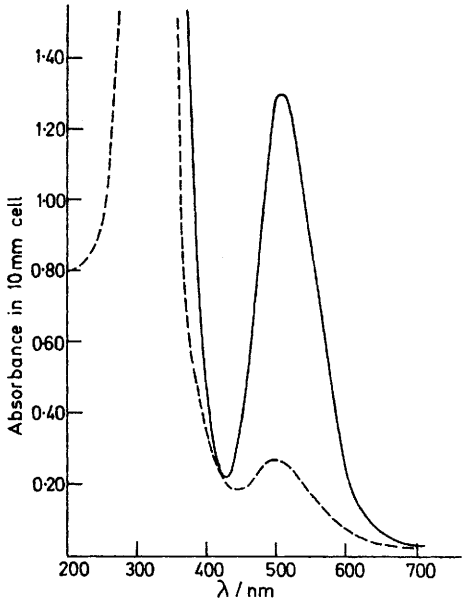

FIGURE 1 Electronic spectra of $[Ni(PEt_3)_4]$ in benzene (1.25×10^{-3} mol dm^{-3}): (——) under argon, (— — —) under CO_2

(*Peroxocarbonato*)*bis*(*tricyclohexylphosphine*)*nickel*(II).—Complex (1) reacted with oxygen at pressure lower than 1 atm and at room temperature, in the solid state or in solution, to give a nickel(II) peroxocarbonate species (4) *via* insertion of O_2 into the Ni–C bond [equation (4)]. Oxygen uptake by solid samples was

$$\underset{\text{orange}}{[Ni(CO_2)\{P(C_6H_{11})_3\}_2]} + O_2 \longrightarrow \underset{\text{pink}}{[Ni(CO_4)\{P(C_6H_{11})_3\}_2]} \quad (4)$$

followed in a thermostatted cell connected to a manometer. Although the uptake rate was dependent on several factors (amount of complex, O_2 pressure, grinding of the sample, and temperature), the O_2 consumption ceased at a O_2 : Ni mol ratio of 1 : 1 (Figure 2) and no phosphine oxide was detected. The i.r. spectrum of solid (4) (see Table) showed bands in accordance with those reported by Hayward *et al.*[14] for $[M(CO_4)(PPh_3)_2]$ (M = Pd^{II} and Pt^{II}). Determination of the peroxo-group by the same technique used by those workers gave low values as the phosphine was oxygenated by the O_2 group. The same difficulty was encountered by the previous workers.

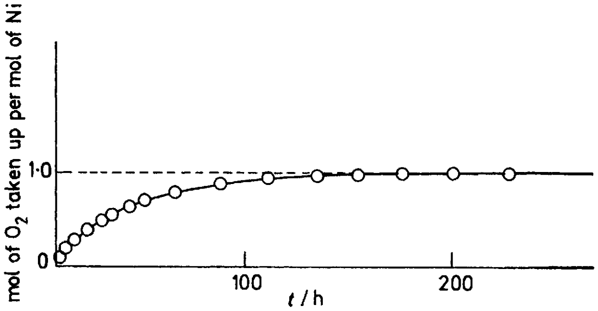

FIGURE 2 Uptake of oxygen by $[Ni(CO_2)\{P(C_6H_{11})_3\}_2]$ in the solid state (37.2 mg of complex, p_{O_2} 222 mmHg, 292 K)

EXPERIMENTAL

All the reactions were carried out in anhydrous solvents which were distilled and stored under argon. Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer, and u.v. and visible spectra on a CF4 Optica instrument. Gas-chromatographic measurements were made with a Carlo Erba model CAT_2 Fractovap connected to a Hewlett-Packard 3380 A integrator. The complexes $[Ni(PEt_3)_4]$, $[Ni(PBu^n{}_3)_4]$, and $[Ni(CO_2)\{P(C_6H_{11})_3\}_2]$ were prepared as reported previously.[1,2]

(*Carbon dioxide*)*bis*(*triethylphosphine*)*nickel*, $[Ni(CO_2)(PEt_3)_2]$ (2).—A solution of $[Ni(PEt_3)_4]$ (1.2 g) in toluene (40 cm^3) was saturated with CO_2 at room temperature and stored at −30 °C for 2 h, then saturated with CO_2 at this temperature and allowed to stand for 12 h. Yellow crystals precipitated and were filtered off at −30 °C under CO_2, washed with cold pentane, and dried *in vacuo* (yield 50% based on Ni). The mother liquor was saturated with CO_2 at −30 °C and, on standing, deposited more product (overall yield 75%), decomp. >134 °C {Found: CO_2 12.85; Ni, 17.3; P, 18.0. Calc. for $[Ni(CO_2)(PEt_3)_2]$: CO_2, 13.0; Ni, 17.3; P, 18.25%}.

(*Carbon dioxide*)*bis*(*tri-n-butylphosphine*)*nickel*, $[Ni(CO_2)(PBu^n{}_3)_2]$ (3).—This complex was similarly prepared from

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[12] C. A. Tolman, *Inorg. Chem.*, 1971, **10**, 1540.

[13] C. A. Tolman, D. H. Gerlach, J. P. Jesson, and R. A. Schunn, *J. Organometallic Chem.*, 1974, **65**, C23.

[14] P. J. Hayward, D. M. Bloke, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, 1970, **92**, 5873.

$[Ni(PBu^n_3)_4]$ in toluene (30 cm^3) saturated with CO_2 at −70 °C (yield 70% based on Ni), decomp. 110—112 °C {Found: CO_2, 8.55; Ni, 11.45; P, 12.0. Calc. for $[Ni(CO_2)(PBu^n_3)_2]$: CO_2, 8.6; Ni, 11.55; P, 12.2%}.

(Peroxocarbonato)bis(tricyclohexylphosphine)nickel(II), $[Ni(CO_4)\{P(C_6H_{11})_3\}_2]$ (4).—(*a*) Finely powdered $[Ni(CO_2)\{P(C_6H_{11})_3\}_2]$ (20—50 mg) was exposed to dry oxygen (100—500 mmHg) in a thermostatted cell (18.4 cm^3) connected to a manometer, while the solid was continually ground and removed by stirring. Oxygen uptake was followed and ceased when a O_2 : Ni mol ratio of 1 : 1 was reached. The pink complex obtained was recovered and analysed.

(*b*) Complex (1) (300 mg) was dissolved in toluene (20 cm^3) in a flask (150 cm^3) at 0 °C and after evacuation dry oxygen was admitted (450 mmHg). The colour of the solution changed rapidly from orange to pink and on cooling to −70 °C the concentrated solution (5 cm^3) deposited a salmon-pink product that was filtered off, washed with pentane, and dried *in vacuo* (yield 80%), decomp. *in vacuo* 140 °C {Found: CO_2, 6.25; Ni, 8.40; P, 8.85. Calc. for $[Ni(CO_4)\{P(C_6H_{11})_3\}_2]$: CO_2, 6.35; Ni, 8.45; P, 8.90%}. The peroxo-group gave up to 45% of the theoretical amount.

Carbon Dioxide Analysis.—Weighed samples (20—30 mg) of the solid complexes were added with benzene (0.1—0.2 cm^3) at −70 °C to a thin-walled ampoule (*ca.* 2 cm^3) under argon. On to the solidified benzene, iodine crystals (or degassed concentrated sulphuric acid, four drops) were deposited and the ampoule was sealed under argon at −70 °C and allowed to reach room temperature, when a reaction took place with vigorous gas evolution. The gas evolved was analysed by breaking the ampoule in a suitable cell attached to a gas chromatograph. The cell was designed so that no solvent or residual iodine vapours could enter the column [length, 3 m; inner diameter, 4 mm; filled with Chromosorb 102; oven temperature, 40 °C; injection port temperature, 25 °C, carrier gas, argon (flow rate, 45 cm^3 min^{-1})]. The absence of other gases (H_2, CO, O_2, N_2, *etc.*) was ascertained by running analyses on a 2-m column of molecular sieves. Heating of the ampoule containing the benzene slurry, after reaction with iodine or H_2SO_4, gave the same results as at room temperature.

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