Carbon Dioxide Induced Metathesis of C≡N and C≡O Triple Bonds of Methyl Isocyanide and Carbon Monoxide

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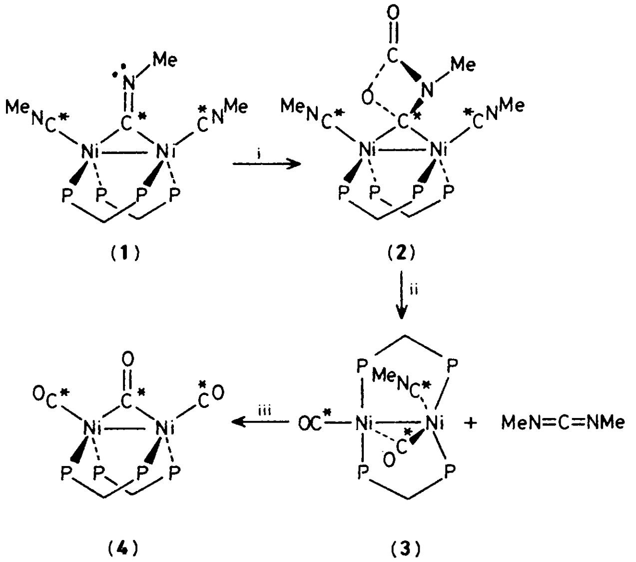
Metathesis of the C≡N triple bonds of the methyl isocyanide ligands of $Ni_2(CNMe)_3(dppm)_2$, (**1**), [dppm = bis(diphenylphosphino)methane] and the C≡O triple bonds of the carbonyl ligands of $Ni_2(CO)_2(CNMe)(dppm)_2$, (**3**), can be achieved thermally or photochemically *via* oxygen atom transfer from carbon dioxide.

The activation of carbon dioxide by transition metal complexes has recently been an area of intense interest.[1] One intriguing line of inquiry involves the use of carbon dioxide as an oxygen atom transfer reagent. However, few precedents for this reaction exist.[2,3] We report herein the direct transfer of two oxygen atoms from carbon dioxide to co-ordinated methyl isocyanide ligands, resulting in the net conversion of CO_2 and two methyl isocyanides to two carbon monoxides and *N,N′*-dimethylcarbodiimide, following the isotopic course of equations (1) and (2).

$$O{=}C{=}O + {:}C^{*}{\equiv}NMe \rightleftarrows O{=}C{=}NMe + {:}C^{*}{\equiv}O \qquad (1)$$

$$MeN{=}C{=}O + {:}C^{*}{\equiv}NMe \rightleftarrows MeN{=}C{=}NMe + {:}C^{*}{\equiv}O \qquad (2)$$

We have previously reported the chemistry and photochemistry of $Ni_2(CNMe)_3(dppm)_2$ (**1**) with CO_2. Either the reaction of (**1**) with liquid CO_2 or photolysis of solutions of (**1**) in the presence of CO_2 (g, 1 atm) affords the CO_2 cycloadduct, $Ni_2(\mu\text{-}CNMe)(CO_2)(CNMe)_2(dppm)_2$ (**2**) [dppm = bis(diphenylphosphino)methane].[3,5] Under an N_2 atmosphere, tetrahydrofuran (THF)–hexane solutions of pure (**2**) deposit dark amber crystals of $Ni_2(\mu\text{-}CO)(CO)(CNMe)(dppm)_2$ (**3**) in quantitative yields (Scheme 1).



Scheme 1. *Reagents and conditions:* i, liquid CO_2, 1400 p.s.i., 24 h, or CO_2 (g, 1 atm), $h\nu$ (λ = 366 nm); ii, N_2, hexane–THF, 7 days; iii, CO_2 (l), 1400 p.s.i., 24 h, all at 25 °C.

The structure of (**3**) is shown in Figure 1.‡ The complex exhibits a *cis–trans* arrangement of the bridging diphosphine

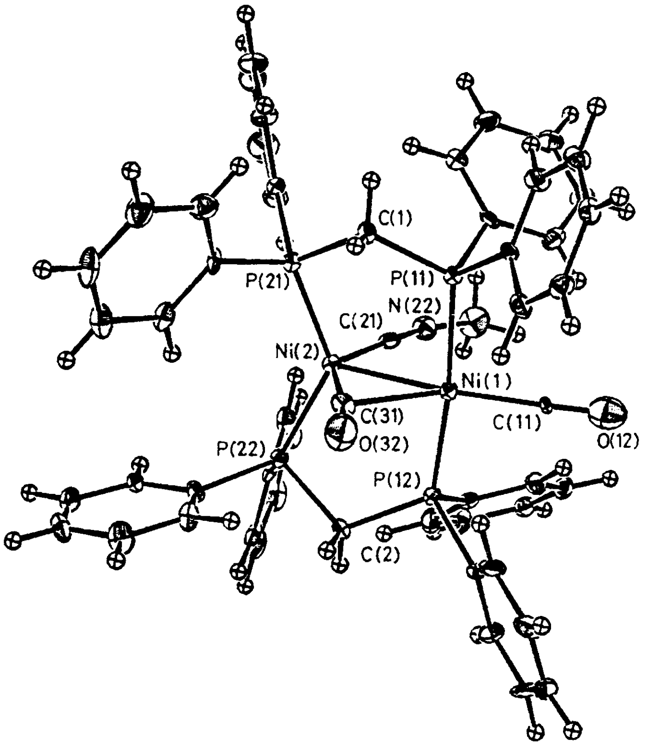


Figure 1. Ortep projection of (**3**). Non-hydrogen atoms are depicted as 50% probability ellipsoids, hydrogen atoms as spheres of arbitrary size. Pertinent distances (Å) and angles (°): Ni(1)–Ni(2), 2.4004(8); Ni(1)–C(11), 1.863(4); Ni(1)–C(31), 2.185(4); Ni(1) ··· C(21), 2.611(5); Ni(2)–C(21), 1.813(4); Ni(2)–C(31), 1.885(4); Ni(2)–Ni(1)–P(11), 85.34(3); Ni(2)–Ni(1)–P(12), 86.06(3); Ni(2)–Ni(1)–C(11), 169.9(1); P(11)–Ni(1)–P(12), 169.25(5); P(11)–Ni(1)–C(11), 93.2(1); P(12)–Ni(1)–C(11), 94.2(1); P(21)–Ni(2)–P(22), 132.78(5); P(21)–Ni(2)–C(21), 105.9(1); P(21)–Ni(2)–C(31), 91.8(1); P(22)–Ni(2)–C(21), 103.3(1); P(22)–Ni(2)–C(31), 93.0(1); C(21)–Ni(2)–C(31), 139.0(2).

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‡ *Crystal data* for (**3**): $Ni_2P_4O_3NC_{58}H_{55}$, M = 1055.41, space group $P\bar{1}$, a = 10.530(2), b = 11.972(3), c = 20.792(4) Å, α = 104.47(2), β = 93.57(2), γ = 95.95(2)°, U = 2514(2) Å^3, Z = 2, D_c = 1.394 g cm^{-3}, $F(000)$ = 1100, μ = 24.97 cm^{-1}. 6530 Unique reflections observed, of which 5201 had $I > 3\sigma(I)$, θ–2θ scans over the range $3 < 2\theta < 112°$, graphite monochromator, Cu-K_α radiation (λ = 1.54181 Å), T = −152 °C, crystal dimensions 0.31 × 0.18 × 0.15 mm. Data were collected on an Enraf-Nonius CAD4 diffractomer and an empirical absorption correction was applied. The structure was solved using direct methods and refined using the Enraf-Nonius SDP program to R = 0.055, R_w = 0.075, p = 0.070. The largest shift/e.s.d. in the final cycle of least-squares refinement in any parameter was 0.12 and the goodness of fit was 1.664. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ligands [P(11)–Ni(1)–P(12) 169.25(5)°, P(21)–Ni(2)–P(22) 132.78(5)°] with a Ni–Ni separation of 2.4004(8) Å, consistent with a Ni–Ni single bond. The μ-CO ligand is distinctly unsymmetrical with Ni(1)–C(3) 2.185(4) Å and Ni(2)–C(31) 1.885(4) Å. The co-ordination geometries about the metal centres may be best described as pseudo-tetrahedral about Ni(2) with bond angles ranging from 135.0(2) to 91.8(1)°, and pseudo-square planar about Ni(1) with bond angles ranging from 85.34(3) to 94.2(1)°. These differences in co-ordination geometries about the two metal centres impart a grossly asymmetric overall structure to the complex. The 'mixed geometry' structure exhibited here appears to be quite common for binuclear nickel complexes.[3a,5,6]

Complex (**3**) was also satisfactorily characterized by elemental analysis, i.r., and n.m.r. spectroscopy; i.r. (KBr): ν(CN) 2109s $\mathrm{cm^{-1}}$, ν(CO) 1939s, 1773m $\mathrm{cm^{-1}}$; ^{31}P n.m.r. (80.9 MHz, CD_3CN, 25 °C, relative to 85% H_3PO_4 external): δ 22.63 (AA′BB′) p.p.m. ^{1}H n.m.r. (200 MHz, [$^2H_8$]-THF, 25 °C): δ 2.31 (s, 3H, $CNCH_3$), 2.54 [br. m, 4H, P–CH_2–P], 7.14 [m, 40H, C_6H_5–].

The structure of (**3**) reveals the presence of two carbon monoxide ligands, derived from decomposition of the CO_2 cycloadduct (**2**). Isotope labelling studies with ^{13}CNMe indicate that the CO carbon atoms of (**3**) trace their origin uniquely to the labelled CNMe carbon atoms of (**1**) or (**2**). The fate of the CO_2 carbon atom has been determined to be the formation of polymeric *N,N′*-dimethylcarbodiimide, which was detected by i.r. spectroscopy.[7] The overall conversion (**1**) → (**2**) → (**3**) is therefore a C≡N/C≡O triple bond metathesis mediated by carbon dioxide. In the presence of CO_2 (Scheme 1), the CNMe ligand of (**3**) undergoes a third metathetical reaction to produce $Ni_2(CO)_3(dppm)_2$, (**4**).[4]

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