fragment becomes joined to another unsaturated ligand in the coordination sphere of a transition-metal atom.

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Synthesis of $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ and Its Reactivity toward CO_2, CO, and CH_2O. First Observation of a Carbonyl-Carbonate Oxidative Conproportionation Mediated by a Transition-Metal Complex

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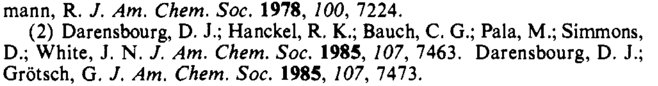
The insertion of small molecules into transition-metal–carbon bonds plays a prominent role in a number of important stoichiometric and catalytic processes. Among these reactions, those involving carbon monoxide have been extensively studied[1] both from a synthetic and a mechanistic point of view. Less well-studied, although of increasing interest,[2] are the insertions of carbon dioxide, while only a few examples of formaldehyde insertion[3] have been reported to date. In this paper we wish to report our findings on the insertion chemistry and related reactions of these molecules with the nickelacyclopentene[4] complex $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**1**). The reactions studied are summarized in Scheme I.

Complex **1** is formed in good yields[5] by the reaction of $NiCl_2(PMe_3)_2$ with 2 equiv of $Mg(CH_2CMe_2Ph)Cl$, *in the presence of traces of* I^- (eq 1).



$$NiCl_2(PMe_3)_2 + 2Mg(CH_2CMe_2Ph)Cl \xrightarrow{I^-} (Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4) + 2MgCl_2 \quad (1)$$

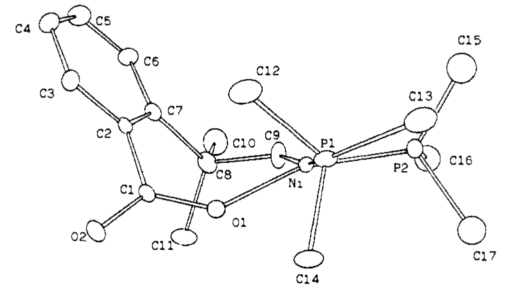
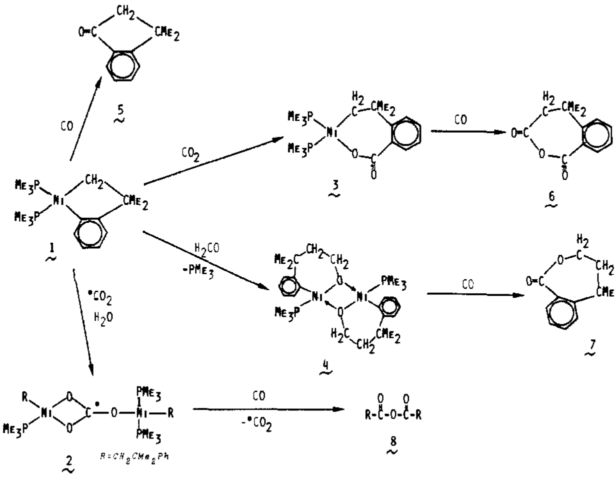


Figure 1. ORTEP diagram for **3** and atom labeling scheme. Important bond distances and angles: Ni–P1 = 2.291 (4), Ni–P2 = 2.143 (4), Ni–O1 = 1.877 (9), Ni–C9 = 1.96 (1) Å; C1–O1–Ni = 137.4 (9)°.

Scheme I



A number of experimental observations made during the progress of this work indicate[6] a catalytic role for I^-, but no mechanistic information on this intringuing reaction is yet available. Although **1** does not react with water under normal conditions, a fast protolytic cleavage of the Ni–aryl carbon bond takes places in the presence of wet CO_2, with quantitative formation[9] of the dimetallic carbonate **2**, which contains a $\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3$ bridge (eq 2). This coordination mode of the bridging carbonate ligand has some precedents in the literature.[11] If the reaction with carbon dioxide is carried out under very strict anhydrous conditions, the yellow nickelalactone **3**, i.e., the normal

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[1] Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. Casey, C. P.; Baltusis, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 6347. Jablonski, C. R.; Wang, Y. *Inorg. Chem.* **1982**, *21*, 4037. Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224.

[2] Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463. Darensbourg, D. J.; Grötsch, G. *J. Am. Chem. Soc.* **1985**, *107*, 7473.

[3] (a) Tikkanen, W. R.; Pettersen, J. L. *Organometallics* **1984**, *3*, 1651. (b) Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576. (c) Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1983**, *255*, C31.

[4] A related nickelabenzocyclopentene complex has been recently obtained via a different route: Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

[5] A cold (−70 °C) stirred suspension of $NiCl_2(PMe_3)_2$ (1.68 g, ca. 6 mmol) in 70 mL of Et_2O was treated with $Mg(CH_2CMe_2Ph)Cl$ (15.4 mL of a ca. 0.78 M Et_2O solution) in the presence of MgI_2 (two drops of a ca. 7×10^{-2} M Et_2O solution). After 2 h of stirring at room temperature and following normal workup, complex **1** can be crystallized as orange prisms from Et_2O or petroleum solutions in ca. 75% yield. If the activation of Mg during the Grignard synthesis is accomplished by addition of I_2, no additional I^- is required for the metalation reaction to take place.

[6] In the absence of I^-, only the monoalkyl $NiCl(CH_2CMe_2Ph)(PMe_3)_2$[7] is formed. The cyclometalated complex **1** cannot be detected even after stirring for 24 h at room temperature in the presence of 2–3 equiv of the Grignard reagent. It is possible that free I^- accelerates the second alkylation to give the unobserved $Ni(CH_2CMe_2Ph)_2(PMe_3)_2$ which readily undergoes a δ-elimination[8] reaction to produce **1**. The intermediacy of a dialkylnickel(II) species is supported by the observation that $Ni(CH_2CMe_2Ph)_2$ (tmed)[7] reacts with PMe_3 to give complex **1**. We are unaware of any previous report of a such dramatic influence of traces of I^- in the behavior of a Grignard reagent.

[7] Carmona, E.; Gonzâlez, F.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1981**, 777.

[8] Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448. Chappell, D. S.; Cole-Hamilton, D. *Polyhedron* **1982**, *1*, 739.

[9] Three drops of water were added to a solution of **1** in Et_2O (0.96 g, ca. 2.8 mmol; 25 mL), and the mixture was pressurized with CO_2 (3 atm). Stirring at room temperature for ca. 15 min and evaporation to dryness furnished yellow microcrystalline **2** in almost quantitative yield. Recrystallization from Et_2O at −20 °C gives analytically pure crystals of **2** in ca. 90% yield. Representative spectroscopic data for **2**: $^{31}P\{^1H\}$ NMR (C_6D_6, 21 °C) δ −3.8 (br s, P_A) and −17.3 (br s, P_B); $^{13}C\{^1H\}$ NMR (C_6D_6, 21 °C) δ 12.3 (br s, PMe_3), 18.0 (v br, $NiCH_2CMe_2$), 32.5 (s, CH_2CMe_2Ph), 41.0 (s, CH_2CMe_2Ph), 124.6, 126.5, 127.7 (s, C-H Ar), 154.1 (br s, quaternary aromatic carbon), 170.4 (s, CO_3). An exchange process of the PMe_3 ligands probably similar to that observed in a related Rh system[10] could be responsible for the simplicity of the observed spectra. IR (Nujol mull) CO_3 absorption at 1505 cm^{-1}. Anal. Calcd for $C_{30}H_{53}O_3P_3Ni_2$: C, 53.6; H, 7.9; O, 7.1. Found: C, 53.5; H, 7.7; O, 7.9. The Me_3SiCH_2 analogue of **2** has been structurally characterized: Marin, J. M., unpublished results.

[10] Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212.

[11] See for instance: Krogsrud, S.; Komiya, S.; Ito, T.; Ibers, J. A.; Yamamoto, A. *Inorg. Chem.* **1976**, *15*, 2798.

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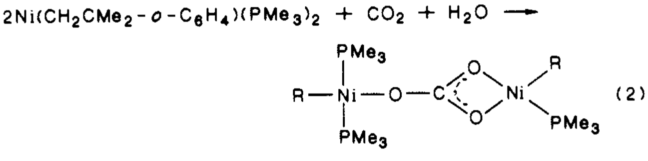
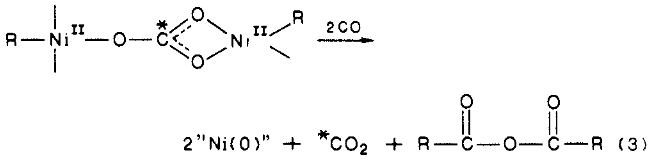


2, R = CH_2CMe_2Ph

CO_2 insertion product into the Ni–aryl carbon bond, is obtained. Complex **3** exhibits a strong IR absorption[12] at ca. 1610 cm^{-1} for the uncoordinated C=O group. The existence of the seven-member nickelalactone unit in the molecule of this compound has been confirmed by X-ray crystallography.[13] A perspective view of the molecular geometry, giving the atom-labeling scheme, is presented in Figure 1, which also includes some important bonding parameters.

The reaction of formaldehyde with transition-metal complexes, and in particular formaldehyde insertion into M–L bonds, is receiving increasing attention in view of the intermediary role played by this molecule in CO reduction.[15] Both the insertion of the CH_2O unit into M–H bonds[16] and the related insertion into M–C bonds, which has been suggested[3a] as a possible propagation step in Fischer–Tropsch chemistry, are still rather uncommon reactions. Addition of aqueous formaldehyde, or preferably paraformaldehyde, to tetrahydrofuran solutions of **1** causes insertion of the CH_2O unit into the *nickel–carbon alkyl bond*, with formation of the oxynickelacycloheptene complex **4**.[17]

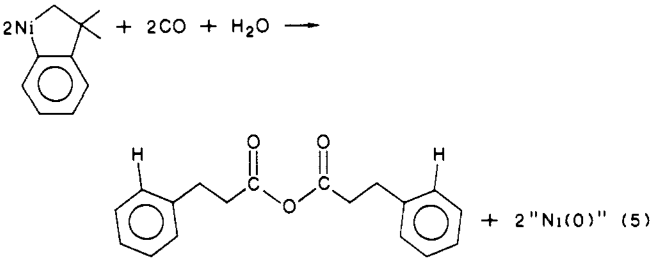
Several organic materials can be derived, in virtually quantitative yields (by NMR spectroscopy), from complexes **1–4** by carbonylation. Thus, **1** produces the cyclic ketone **5**, while **3** and **4** afford anhydride **6** and lactone **7**, respectively. Interestingly, the reaction of the carbonate **2** with carbon monoxide takes place with reduction to Ni(0) ($Ni(CO)_2(PMe_3)_2$ plus $Ni(CO)_3(PMe_3)$), formation of anhydride **8**, and evolution of carbon dioxide (eq 3).



Isotopic labeling studies using complex **2**, ^{13}C enriched in the carbonate ligand, clearly demonstrate that the evolved CO_2 derives exclusively from the carbonate group. In a formal sense, eq 3 represents a metal-promoted oxidative conproportionation of carbonate and carbonyl ligands to produce two molecules of carbon dioxide (eq 4). One of these is evolved as free CO_2 while the

$$CO_3^{2-} + CO - 2e = 2CO_2 \qquad (4)$$

second is "functionalized" into the anhydride functionality. Although the opposite reaction, namely, reductive disproportionation of carbon dioxide, is a commonly observed process in transition-metal–carbon dioxide chemistry, to the best of our knowledge eq 3 represents the first example of a carbonate and a carbon monoxide conproportionation induced by a transition-metal complex.[18] Moreover, the simultaneous consideration of eq 2 and 3 reveals that the overall process is a CO_2-mediated hydrocarbonylation of **1** to produce anhydride **8**, as in eq 5.



Further studies on this and related carbonate complexes are in progress to ascertain the generality of this reaction and its potential synthetic applicability.

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Supplementary Material Available: Tables of final fractional coordinates, thermal parameters, and bond distances and angles for 3 (4 pages); table of observed and calculated structure factors for 3 (22 pages). Ordering information is given on any current masthead page.

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(12) Compound **3** seems to exist in two interconvertible forms displaying $\nu C{=}O$ at 1610 and 1580 cm^{-1}.

(13) Crystal data for **3**, $C_{17}H_{30}P_2O_2Ni$: M_r = 387.08, orthorhombic, space group $P_{2_12_12_1}$; a = 10.139 (3) Å, b = 10.543 (2) Å, c = 18.665 (3) Å v = 1995.2 (8) Å^3, Z = 4, D_{calcd} = 1.29 g cm^3, $F(000)$ = 824, μ (Mo Kα) = 11.4 cm^{-1}. A yellow prismatic crystal (0.5 × 0.3 × 0.2 mm) was sealed under N_2 in a glass capillary, and data were collected on a Enraf-Nonius CAD4-F diffractometer. The structure was solved by heavy atom methods; 3267 independent reflections were measured of which 2020 were considered observed after the criterion $I > 3\sigma(I)$ and used in the refinement with anisotropic parameters for all non-H atoms except the methyl carbons attached to phosphorus (2). Unit weights were used (no trend in ΔF vs. F_o or $\sin \theta/\lambda$ was observed), and at convergence, R_F = 0.067. An absorption correction was applied.[14]

(14) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

(15) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

(16) Wayland, B. B.; Woods, B. A.; Minda, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634.

(17) A solution of **1** (1.56 g, ca. 4.55 mmol) in THF (40 mL) is stirred at room temperature with an excess of solid paraformaldehyde for ca. 4 h. The yellow suspension obtained is evaporated to dryness. Crystallization from Et_2O/petroleum ether (1:1 mixture) at −20 °C afforded **4** as yellow microcrystals in ca. 80% yield. This compound exists in solution in two isomeric forms in ca. 2:1 ratio. This possibly arises from the relative positions of the oxyalkyl chains with respect to the Ni_2O_2 ring. Some spectroscopic data corresponding to the major isomer are as follows: $^{31}P\{^1H\}$ NMR (C_6D_6, 21 °C) δ −12.7 s; $^{13}C\{^1H\}$ NMR (C_6D_6, 21 °C) δ 13.7 (d, PMe_3, $^1J_{CP}$ = 28 Hz), 31.6, 35.2 (s, diastereotopics CMe_2), 37.7 (s, CMe_2), 50.4 (s, CCH_2), 65.5 (s, OCH_2), 147.8 (d, Ar C bound to Ni, $^2J_{CP}$ = 42.1 Hz). M_r (cryoscopically, C_6H_6), calcd for $C_{28}H_{46}O_2P_2Ni_2$, 593; found, 530. Anal. Calcd for $C_{28}H_{46}O_2P_2Ni_2$: C, 56.6; H, 7.7. Found: C, 56.4; H, 7.7.

(18) Organic allyl alkyl carbonates are known to undergo a Pd-catalyzed decarboxilation–carbonylation process to yield unsaturated esters. Tsuji, J.; Sato, K.; Okumoto, H. *J. Org. Chem.* **1984**, *49*, 1341.

Inside–Outside Stereoisomerism: The Synthesis of *trans*-Bicyclo[5.3.1]undecan-11-one[1]

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We have reported that the intramolecular photoaddition of dioxolenones to alkenes, i.e., **1** → **3**, leads to the formation of six-, seven- and eight-membered rings in good yield.[5] We describe

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(1) Winkler, J. D. Presented in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 8–13, 1985; paper ORGN 205.

(2) Recipient of a Merck Grant for Faculty Development, 1985–1986.

(3) National Institutes of Health Predoctoral Trainee (GM07148).

(4) Author to whom correspondence regarding the X-ray structure of **11** should be addressed.

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