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Synthesis and X-ray Structure of the Nickelabenzocyclopentene Complex $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$. Reactivity Toward Simple, Unsaturated Molecules and the Crystal and Molecular Structure of the Cyclic Carboxylate $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4C(O)O)$

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Abstract: Facile cyclometalation to the nickelacyclopentene complex $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (**1**) occurs upon alkylation of $NiCl_2(PMe_3)_2$ with 2 equiv of $Mg(CH_2CMe_2Ph)Cl$, in the presence of traces of I^-. Compound **1** has been fully characterized by spectroscopic and X-ray studies. Its characteristic insertion chemistry has also been investigated. For carbon monoxide and diphenylacetylene, insertion is followed by rapid reductive elimination which affords the cyclic ketone **10** and the dihydronaphthalene **6** as the only organic products. Formaldehyde inserts into the Ni–C(alkyl) bond and produces the oxynickelacycloheptene derivative $[(Me_3P)Ni(OCH_2CH_2CMe_2\text{-}o\text{-}C_6H_4)]_2$ (**3**), but carbon dioxide gives the nickelalactone species $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4C(O)O)$ (**2**), i.e., the product of the insertion into the Ni–C(aryl) bond, as demonstrated by single-crystal X-ray structural analysis. Compounds **2** and **3** can be readily carbonylated to anhydride **7** and lactone **8**, respectively. Action of CO_2 on **1**, in the presence of water, induces protolytic cleavage of the Ni–C(aryl) bond and formation of the binuclear, carbonate-bridged complex, $(Me_3P)_2(R)Ni(\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3)Ni(R)PMe_3$ ($R = CH_2CMe_2Ph$, **5**), whose carbonylation allows observation of the first carbonyl–carbonate oxidative conproportionation reaction, $CO + CO_3^{2-} - 2e = 2CO_2$, induced by a transition-metal complex. Compound **1** crystallizes in the space group $P2_1/c$ with cell dimensions $a = 8.782$ (2), $b = 18.792$ (7), and $c = 12.290$ (4) Å, $\beta = 110.63$ (2)°, and $D_{calcd} = 1.20$ g cm^{-3} for $Z = 4$. **2** is orthorhombic, space group $P2_12_12_1$, with cell dimensions $a = 10.139$ (3), $b = 10.543$ (2), and $c = 18.665$ (3) Å and $D_{calcd} = 1.29$ g cm^{-3} for $Z = 4$.

The insertion of small molecules into transition-metal–carbon bonds is a fundamental reaction in organotransition metal chemistry.[2] Its investigation in many systems is however hampered by the very facility of some decomposition reactions. In particular, the β-elimination of a metal hydride, which is a ubiquitous reaction in transition-metal alkyl chemistry, severely limits the scope of insertion reactions and other chemistry to systems that are stabilized with respect to this common decomposition pathway. Early work by Whitesides et al.[3] demonstrated that the β-hydrogen elimination can be suppressed, or at least hindered, by formation of metalacyclic complexes, which, in general, display thermal stability much higher than that of the acyclic analogues.

Transition-metal metalacycles have become important organometallic species in recent years,[4,5] and sufficient evidence has been gained to conclusively demonstrate their participation in a number of catalytic reactions, such as alkene metathesis, oligomerizations, or cycloadditions.[6] Metalacyclic compounds have been obtained, among other routes,[7,8] by intramolecular activation of a distal C–H bond of a coordinated ligand.[9-14] For example, $Ru_2(O_2CCH_3)_4Cl$ has been shown to react with $Mg(CH_2Bu^t)_2$, in the presence of PMe_3,[10] with production of $(Me_3P)_4Ru(CH_2CMe_2CH_2)$. More forcing conditions are required for the formation of the related complexes $(Et_3P)_2Pt(CH_2CMe_2CH_2)$[11] and $Pt(CH_2C_6H_4\text{-}o\text{-}CH_2)(PR_3)_2$,[12] by γ- and δ-hydrogen abstraction, respectively. If the coordinated ligand is an alkyl group that has distal aromatic C–H bonds, a metalacyclic compound containing both a M–C(alkyl) and a M–C(aryl) bond may be obtained. Prior to the start of this work the production of the

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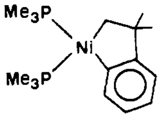
related $\overline{\mathrm{Ir(CH_2CMe_2\text{-}}o\mathrm{\text{-}C_6H_4}}\mathrm{)H(PMe_3)_3}$[13] had been published, and during the progress of this work other similar metalacyclopentene complexes[14,15] have been obtained by this and other synthetic procedures.

During our own investigations on the chemistry of alkyl and other organometallic compounds of nickel,[16] we have observed formation of the nickelacyclopentene complex $\overline{\mathrm{(Me_3P)_2Ni\text{-}(CH_2CMe_2\text{-}}o\mathrm{\text{-}C_6H_4}}\mathrm{)}$ (**1**), which contains a Ni–C(alkyl) and a Ni–C(aryl) bond constrained to a cis arrangement by the nature of the cyclic ligand. The vast majority of the alkylaryl complexes of nickel reported to date have trans geometry,[17] and when the alkyl and aryl groups are forced to be in a cis position, i.e., by action of a chelating phosphine, as in $\mathrm{Ni(CH_3)C_6H_5(dmpe)}$,[17a] a marked decrease in the thermal stability is observed. Isolation of complex **1** provides therefore a unique opportunity to investigate the chemistry of *cis*-alkylaryl complexes of nickel. In this paper we report the preparation and structural characterization of **1** and the study of its reactivity toward CO, CO_2, CH_2O and PhC≡CPh. Part of this work has been briefly communicated.[18]



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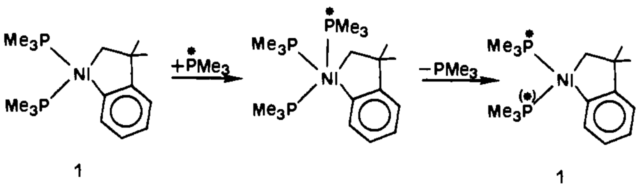
Results and Discussion

Synthesis and Molecular Structure of the Nickelacyclopentene Complex $\overline{\mathrm{(Me_3P)_2Ni(CH_2CMe_2\text{-}}o\mathrm{\text{-}C_6H_4}}\mathrm{)}$ (1). Some time ago we reported that the reaction of $\mathrm{NiCl_2(PMe_3)_2}$ with (2-methyl-2-phenylpropyl)magnesium chloride (neophylmagnesium chloride) affords the red-brown monoalkyl *trans*-$\mathrm{Ni(CH_2CMe_2Ph)Cl(PMe_3)_2}$.[16a] Further alkylation to the dialkyl, $\mathrm{NiR_2(PMe_3)_2}$, does not take place, even in the presence of a large excess of the Grignard reagent. During studies aimed at the investigations of the chemical properties of the monoalkyl, the high-yield production of a different compound, **1**, has sometimes been observed. Microanalytical and cryoscopic molecular weight determinations, along with NMR data (see below), indicate this complex is a nickelacyclopentene species, formed as a result of an orthometalation of the neophyl ligand.[13,14] The synthesis of complex **1** seemed to occur rather unpredictibly and attempts to reproduce it, under apparently the same experimental conditions, led often instead to the alkyl $\mathrm{Ni(CH_2CMe_2Ph)Cl(PMe_3)_2}$. It was soon realized that cyclometalated **1** can only be obtained if the magnesium used for the Grignard synthesis had been activated by addition of iodine, i.e., the cyclometalation reaction requires traces of I^- (or MgI_2). Although we have not carried out detailed studies on the mechanism of this reaction, this, to our knowledge unprecedented iodide effect, is catalytic, as shown by the following experimental observations: two parallel reactions of $\mathrm{NiCl_2(PMe_3)_2}$ (ca. 1 mmol) with 2–3 equiv of $\mathrm{Mg(CH_2CMe_2Ph)Cl}$ (freshly prepared without magnesium activation by I_2) were run, with addition to one of them of 0.1 mL of a ca. 6×10^{-2} M solution of MgI_2. After similar workup, the reaction carried out in the presence of MgI_2 furnished high yields of **1** while the other provided only the monoalkyl $\mathrm{Ni(R)Cl(PMe_3)_2}$. Formation of **1** can therefore be represented as in eq 1.

Scheme I



$$\mathrm{NiCl_2(PMe_3)_2} + 2\mathrm{Mg(CH_2CMe_2Ph)Cl} \xrightarrow{[\mathrm{I^-}]} \mathbf{1} + \mathrm{C_6H_5CMe_3} + 2\mathrm{MgCl_2} \quad (1)$$

The intermediary role of the monoalkyl is demonstrated by its facile cyclometalation by $\mathrm{Mg(CH_2CMe_2Ph)Cl}$, in the presence of MgI_2. On the other hand, the monoalkyl does not cyclometalate by action of the basic reagents $\mathrm{LiN(SiMe_3)_2}$, $\mathrm{LiBu^n}$, or Na–Hg and this clearly argues in favor of the cyclometalation proceeding, as for other related systems,[9–12,14] by δ-hydrogen abstraction from an unstable dialkyl $\mathrm{Ni(CH_2CMe_2Ph)_2(PMe_3)_2}$. Strong support for this proposal comes from the observation that **1** is readily formed by addition of PMe_3 to the unstable, but isolable, dialkyl $\mathrm{Ni(CH_2CMe_2Ph)_2(L\text{-}L)}$[16b] (L-L = *N,N,N′,N′*-tetramethylethylenediamine), as represented in eq 2. Metalation of a neophyl

$$\mathrm{NiCl_2(py)_4} \xrightarrow[\mathrm{L\text{-}L}]{\mathrm{Mg(CH_2CMe_2Ph)Cl}} \mathrm{Ni(CH_2CMe_2Ph)_2(L\text{-}L)} \xrightarrow{\mathrm{PMe_3}} \mathbf{1} \quad (2)$$

ligand in iridium[13] and platinum[14] complexes takes place by oxidative addition of a δ-C–H bond to the metal center. This does not seem likely in the present system since it would imply the formation of a Ni(IV) intermediate. A more plausible pathway for the C–H activation process involves[13] hydrogen abstraction by an incipient radical, in a four-centered transition state, without change in the oxidation state of the nickel center.

Complex **1** is an orange solid which provides large, very well formed, prisms by crystallization from diethyl ether. It is only partially soluble in petroleum but very soluble in other common organic solvents. The compound decomposes rapidly upon exposure to air, both as a solid and in solution. NMR data are in accord with the proposed structure, but due to fluxionality, variable-temperature NMR spectra were needed. In the room-temperature $^{13}C\{^1H\}$ NMR spectrum, a broad singlet at 16.8 ppm is observed for the PMe_3 ligands, a singlet at 52.4 ppm for the methylene carbon, Ni–CH_2, and a very broad resonance at ca. 171.5 ppm for the quaternary aromatic carbon atom bonded to nickel. Upon being cooled at −70 °C, the phosphine ligands become inequivalent, but fluxionality persists and the nickel-bound methylene and aromatic carbons couple only with one of the phosphorus nuclei. The loss of coupling at room temperature and above suggests that the fluxional process implies PMe_3 dissociation, and since addition of PMe_3 to solutions of **1** increases the rate of the PMe_3 interchange, we propose that traces of PMe_3 are responsible for the observed behavior by formation of a five-coordinate, 18-electron intermediate species, as depicted in Scheme

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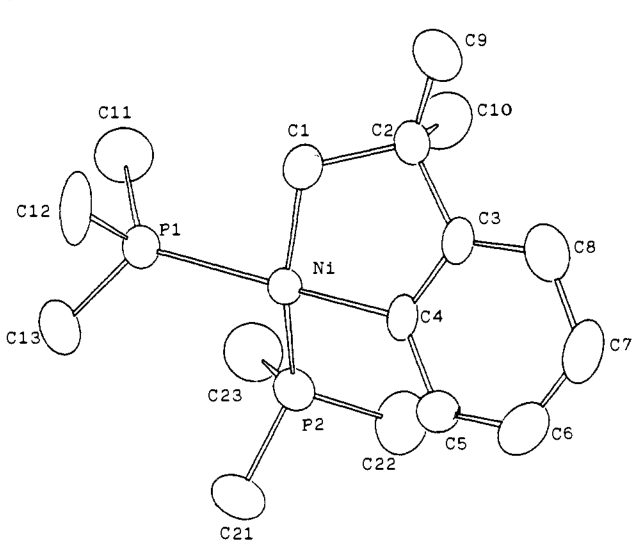

Figure 1. ORTEP diagram for 1 and labeling scheme.

Table I. Summary of Crystal Data

	1	2
empirical formula	$C_{16}H_{30}P_2Ni$	$C_{17}H_{30}P_2O_2Ni$
color	yellow-orange	yellow
space group	$P2_1/c$	$P2_12_12_1$
cell dimensions		
a, Å	8.782 (2)	10.139 (3)
b, Å	18.792 (7)	10.543 (2)
c, Å	12.290 (4)	18.665 (3)
α, deg	90.00 (0)	90.00 (0)
β, deg	110.63 (2)	90.00 (0)
γ, deg	90.00 (0)	90.00 (0)
Z	4	4
V, Å^3	1898 (1)	1995.2 (8)
D_{calcd}, g/cm^3	1.20	1.29
wavelength, Å	0.71069	0.71069
temp, °C	22	22
M_w	343.1	387.08
linear abs coeff, cm^{-1}	11.8	11.4
2θ range, deg	0–44	1–60
no. of unique data	2606	3267
no. of obsd data, $I > 3\sigma(I)$	1439	2020
$R(F)$	0.077	0.067
$R_w(F)$	0.090	0.085

1. The two coordinated PMe_3 ligands should exchange at different rates. In the −70 °C $^{13}C\{^1H\}$ NMR spectrum, the $Ni-CH_2$ and the Ni–C(aromatic) carbon atoms neatly couple to only one of the ^{31}P nuclei, with the very different coupling constants of 16 and 79 Hz, respectively. The former is typical of cis $^2J_{PC}$, while the latter is characteristic of a trans coupling.[28] It seems that, at this temperature, the PMe_3 ligand in trans with respect to the $Ni-CH_2$ bond is still undergoing fast exchange, while for the other phosphine ligand the rate of exchange is slower than the NMR time scale. In accord with this, the two singlets at −5.1 and −11.4 ppm, observed in the $^{31}P\{^1H\}$ NMR of 1 recorded at −70 °C, convert into two broader signals in the spectrum of approximately equimolar solutions of 1 and PMe_3, at the same temperature. The former has a chemical shift similar to the low-field ^{31}P resonance in pure 1, while for the latter the chemical shift is at an average position between free PMe_3 (−63 ppm) and the high-field resonance in 1. The higher trans effect of the alkyl groups with respect to the aryls may be invoked to account for this behavior. No further changes in the NMR spectrum of 1 can be observed upon cooling at −90 °C.

Formulation of 1 as a nickelacyclopentene complex has been confirmed by a single-crystal X-ray diffraction study. Figure 1 shows an ORTEP perspective view, including the atom numbering scheme; a summary of crystal structural data and bond distances and angles is collected in Tables I and II. Details of the structure determination are given in the Experimental Section. The nickel atom is in a distorted square-planar environment, with the phosphine ligands constrained to a cis geometry by the chelating nature of the organic fragment. The steric requirements of the aromatic ring of the metalacycle open up the corresponding C(4)–Ni–P(2) angle to 96.1 (4)°, while the C(1)–Ni–P(1) angle of 88.1 (4)° remains close to the ideal 90° value. The Ni–P bond lengths are equal [2.192 (4) and 2.194 (4) Å] and show no appreciable deviation with respect to other $Ni^{II}-PMe_3$ bonds.[16] There is some tetrahedral distortion manifested by the values of 162.9 (4)° and 153.3 (4)° found respectively for the trans C(1)–Ni–P(2) and C(4)–Ni–P(1) angles. The two Ni–C bonds have somewhat different lengths, with the Ni–C(aryl) distance of 1.93 (1) Å being shorter than the Ni–C(alkyl) at 1.96 (1) Å. Both lengths are in the range found for alkyl and aryl complexes of Ni(II) and compare well with those reported recently by Bennett and coworkers[15] for the related complex $\overline{Ni(CH_2CH_2C_6H_4\text{-}o)}(Cy_2PCH_2CH_2PCy_2)$.

Table II. Bond Distances (Å) and Angles (deg) for 1

Bond Distances			
Ni–P(1)	2.193 (4)	C(1)–C(2)	1.54 (2)
Ni–P(2)	2.193 (4)	C(2)–C(3)	1.53 (2)
Ni–C(1)	1.97 (1)	C(2)–C(9)	1.47 (2)
Ni–C(4)	1.93 (1)	C(2)–C(10)	1.58 (3)
P(1)–C(11)	1.86 (3)	C(3)–C(4)	1.39 (2)
P(1)–C(12)	1.80 (2)	C(3)–C(8)	1.39 (2)
P(1)–C(13)	1.83 (1)	C(4)–C(5)	1.42 (2)
P(2)–C(21)	1.84 (2)	C(5)–C(6)	1.35 (2)
P(2)–C(22)	1.83 (2)	C(6)–C(7)	1.36 (2)
P(2)–C(23)	1.86 (2)	C(7)–C(8)	1.40 (3)

Bond Angles			
P(1)–Ni–P(2)	99.5 (2)	C(3)–C(4)–C(5)	116 (1)
P(1)–Ni–C(1)	88.2 (4)	C(4)–C(5)–C(6)	121 (1)
P(1)–Ni–C(4)	153.3 (4)	C(5)–C(6)–C(7)	122 (2)
P(2)–Ni–C(1)	162.9 (4)	C(6)–C(7)–C(8)	119 (1)
P(2)–Ni–C(4)	96.0 (4)	C(3)–C(8)–C(7)	119 (1)
C(1)–Ni–C(4)	80.7 (5)	C(11)–P(1)–C(12)	103.6 (9)
Ni–C(1)–C(2)	110.2 (9)	C(11)–P(1)–C(13)	101.2 (8)
C(1)–C(2)–C(3)	101 (1)	C(12)–P(1)–C(13)	98.9 (7)
C(1)–C(2)–C(9)	112 (1)	C(21)–P(2)–C(22)	101.3 (8)
C(1)–C(2)–C(10)	110 (1)	C(21)–P(2)–C(23)	102.3 (9)
C(2)–C(3)–C(4)	114 (1)	C(22)–P(2)–C(23)	98.6 (9)
C(2)–C(3)–C(8)	123 (1)		

Chemical Properties of 1. The cyclometalated complex 1 exhibits fairly high thermal stability, no decomposition being observed upon heating at temperatures of 70–80 °C. Three major processes are in general responsible for the decomposition of metalacycles:[8] (i) β-hydrogen elimination; (ii) carbon–carbon bond cleavage, with formation of unsaturated hydrocarbons, and (iii) reductive elimination. The first is obviously suppressed by the existence of two methyl substituents at the β-carbon, while the other two pathways are in principle potential routes to rather unaccessible species, benzyne complexes of nickel(0)[15] and cyclobutenes,[19] respectively. No evidence for such decomposition has hitherto been found.

Notwithstanding its thermal stability, complex 1 is a highly reactive molecule which displays a remarkable insertion chemistry. Here we present a full account of studies concerning the reactions of 1 with CO, PhC≡CPh, CO_2, and CH_2O; those with other unsaturated molecules such as CNR, RNCS, CS_2, and COS will be the subject of subsequent publications.

(a) Reaction with Carbon Monoxide. Organometallic compounds of nickel have a very rich carbonylation chemistry,[20] and carbon monoxide insertions into Ni–C bonds have been investigated extensively. Diethyl ether solutions of 1 react rapidly with an excess of carbon monoxide, under ambient conditions, with formation of cyclic ketone 10, eq 3. Since carbonylations are usually faster for alkyl than for aryl groups,[17b,21] it is likely that the reaction proceeds through a cyclic acyl intermediate.[22] To confirm this, 1 was reacted with 1 equiv of the acyl *trans*-Ni-

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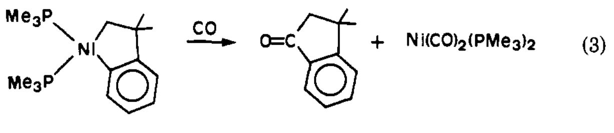
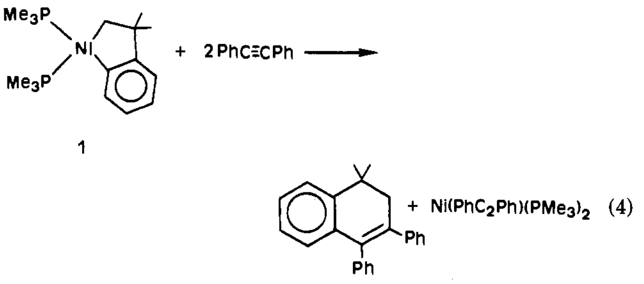


1 10

$(COCH_2SiMe_3)Cl(PMe_3)_2$, which has been demonstrated to act as a mild CO-transfer reagent.[16a] The reaction was however very complex, and in addition to the alkyl, *trans*-$Ni(CH_2SiMe_3)Cl(PMe_3)_2$, and other unidentified compounds, the products of the reductive elimination, $Ni(CO)(PMe_3)_3$ and ketone **10**, were obtained. Conclusive evidence for the mode of insertion of CO comes from the result of the sequential insertion of this molecule and CS_2. Reaction of **1** with CO and CS_2, in either order, provides the dithioanhydride $O{=}\overline{CCH_2CMe_2\text{-}o\text{-}C_6H_4C(S)S}$ as the sole organic product. Preliminary work from this laboratory has conclusively demonstrated[23] that CS_2 inserts exclusively into the Ni–C(aryl) bond of **1**.

(b) Reaction with PhC≡CPh. The insertion of an alkyne into a transition-metal–carbon bond is a fundamental reaction of considerable synthetic utility, which has been studied in detail for alkyl and acyl derivatives of various transition metals.[24] Complex **1** reacts with 2 equiv of PhC≡CPh with quantitative formation of the known alkyne derivative $Ni(PhC{\equiv}CPh)(PMe_3)_2$[25] and the dihydronaphthalene **6**, eq 4. No side products can be detected



1

6

and yields of pure crystalline **6** are ~80%. In view of the scarcity of preparative routes leading to dihydronaphthalenes,[26] the synthetic utility of this simple reaction becomes evident. The development of a general synthetic procedure to dihydronaphthalene derivatives is beyond the scope of the present work, but nevertheless, it is worth discussing at this point that the above reaction suffers from two important synthetic disadvantages: (i) of the two moles of the often rather unaccessible and otherwise expensive alkyne, only one becomes incorporated into the organic functionality and it is therefore synthetically useful; (ii) the alkyne compounds, $Ni(RC{\equiv}CR')(PMe_3)_2$, are frequently thermally unstable[25] and their decomposition may considerably hinder isolation of the pure dihydronaphthalene. These difficulties can be overcome by carrying out the insertion reaction in the presence of PPh_3, which successfully competes with the alkyne for the trapping of the $Ni(PMe_3)_2$ fragment, eq 5. If methanol is used

$$\mathbf{1} + PhC{\equiv}CPh + 2PPh_3 \rightarrow Ni(PMe_3)_2(PPh_3)_2 + \mathbf{6} \quad (5)$$

as a solvent, the Ni(0) product quantitatively precipitates and **6** can be isolated from the supernatant solution.

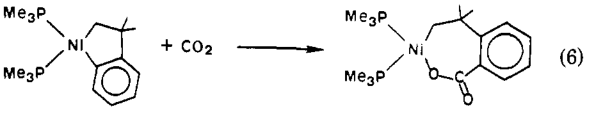
In an attempt to ascertain the insertion mode of PhC≡CPh, **1** was treated with 1 equiv of PhC≡CPh at −70 °C. The reaction mixture was slowly warmed until room temperature and the course of the reaction followed by ^{31}P NMR spectroscopy. No intermediate species was detected, and when the reaction was complete, the reductive elimination products (eq 4) and unreacted **1** (half of the original amount used) were obtained. The insertion does not occur at temperatures below −20 °C, and above this temperature, reductive elimination proceeds faster than insertion.

(c) Carbon Dioxide Insertion. Numerous insertion reactions of CO_2 into transition-metal–carbon bonds have been reported in the literature in recent years.[27] The formation in this reaction of a carbon–carbon bond, with increase of the chain length, coupled with the possibility of reductive elimination at the metal with liberation of the CO_2-containing organic product, provides a convenient route for the conversion of carbon dioxide into useful organic chemicals.[27a] Insertion of CO_2 into metalacycles gains additional importance in view of their implication in many transition-metal catalytic reactions.[6]

Table III. Bond Distances (Å) and Angles (deg) for **2**

Bond Distances			
Ni–P(1)	2.291 (4)	C(1)–C(2)	1.546 (18)
Ni–P(2)	2.143 (4)	C(2)–C(3)	1.363 (20)
Ni–O(1)	1.877 (9)	C(2)–C(7)	1.418 (18)
Ni–C(9)	1.959 (14)	C(3)–C(4)	1.383 (24)
P(1)–C(12)	1.833 (14)	C(4)–C(5)	1.331 (27)
P(1)–C(13)	1.848 (19)	C(5)–C(6)	1.328 (24)
P(1)–C(14)	1.861 (22)	C(6)–C(7)	1.372 (20)
P(2)–C(15)	1.844 (22)	C(7)–C(8)	1.603 (21)
P(2)–C(16)	1.720 (22)	C(8)–C(9)	1.520 (19)
P(2)–C(17)	1.902 (21)	C(8)–C(10)	1.546 (18)
O(1)–C(1)	1.274 (15)	C(8)–C(11)	1.556 (25)
O(2)–C(1)	1.222 (16)		
Bond Angles			
O(1)–Ni–C(9)	94.5 (5)	O(2)–C(1)–C(2)	117.4 (11)
P(2)–Ni–C(9)	86.7 (4)	O(1)–C(1)–C(2)	119.7 (11)
P(2)–Ni–O(1)	162.6 (3)	C(1)–C(2)–C(7)	123.4 (11)
P(1)–Ni–C(9)	169.3 (5)	C(1)–C(2)–C(3)	116.6 (12)
P(1)–Ni–O(1)	81.9 (3)	C(3)–C(2)–C(7)	119.9 (13)
P(1)–Ni–P(2)	99.8 (2)	C(2)–C(3)–C(4)	118.8 (15)
Ni–P(1)–C(14)	127.0 (7)	C(3)–C(4)–C(5)	120.2 (16)
Ni–P(1)–C(13)	109.1 (6)	C(4)–C(5)–C(6)	122.8 (17)
Ni–P(1)–C(12)	112.3 (5)	C(5)–C(6)–C(7)	120.1 (15)
C(13)–P(1)–C(14)	100.0 (8)	C(2)–C(7)–C(6)	118.2 (12)
C(12)–P(1)–C(14)	102.2 (9)	C(6)–C(7)–C(8)	121.5 (12)
C(12)–P(1)–C(13)	103.4 (8)	C(2)–C(7)–C(8)	120.2 (12)
Ni–P(2)–C(17)	118.9 (6)	C(7)–C(8)–C(11)	113.4 (12)
Ni–P(2)–C(16)	121.4 (8)	C(7)–C(8)–C(10)	109.3 (13)
Ni–P(2)–C(15)	109.2 (7)	C(7)–C(8)–C(9)	110.7 (12)
C(16)–P(2)–C(17)	99.2 (11)	C(10)–C(8)–C(11)	107.4 (12)
C(15)–P(2)–C(17)	91.5 (10)	C(9)–C(8)–C(11)	111.1 (13)
C(15)–P(2)–C(16)	112.8 (10)	C(9)–C(8)–C(10)	104.6 (12)
Ni–O(1)–C(1)	137.4 (9)	Ni–C(9)–C(8)	124.6 (10)
O(1)–C(1)–O(2)	122.9 (12)		

Very carefully dried CO_2 (see Experimental Section) reacts very slowly with the nickelacycle **1**, the reaction requiring stirring at room temperature, for 4–5 days, under 4–5 atm of CO_2, for completion. A yellow precipitate of a microcrystalline complex **2** is formed in high yields (70%). The existence of strong absorptions, centered at ca. 1620 cm^{-1}, in the IR spectrum, and of a ^{13}C resonance at 175.5 ppm suggests the presence of a carboxylate group in the molecule of **2**, as a result of the insertion reaction represented in eq 6. Support for this proposal comes



1 2

from NMR studies (see Experimental Section) and from the results of an X-ray study to be commented on below. Related five- and six-membered nickelacyclolactone complexes have been obtained during the progress of this work by insertion of CO_2 into the nickel–carbon bonds of $Ni(\eta^2\text{-}C_6H_4)(Cy_2PCH_2CH_2PCy_2)$[15] and $(Bu^n{}_3P)_2\overline{Ni(CH_2\text{-}o\text{-}C_6H_4)}$.[28] In addition, other related derivatives have been prepared by the nickel-promoted coupling of CO_2 with unsaturated hydrocarbons.[29] Interestingly, complex **2** can be isolated in two different crystalline modifications displaying slightly different IR spectra but identical NMR features. The complex exhibits fluxionality similar to that described above for **1**.

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(29) See, for example: (a) Burkhart, G.; Hoberg, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 76. (b) Hoberg, H.; Schaefer, D.; Burkhart, G.; Krüger, C.; Romão, M. J. *J. Organomet. Chem.* **1984**, *266*, 203. (c) Hoberg, H.; Peres, Y.; Krüger, C.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 771.

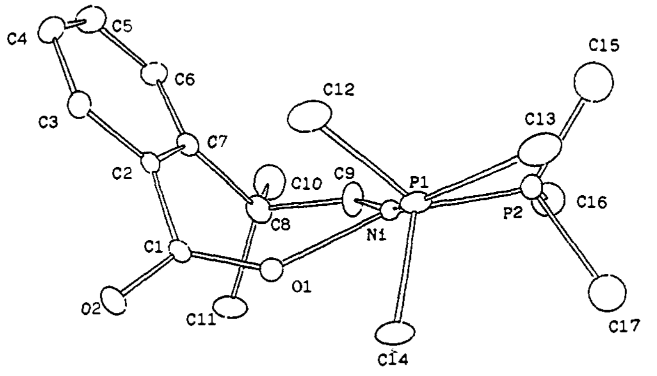


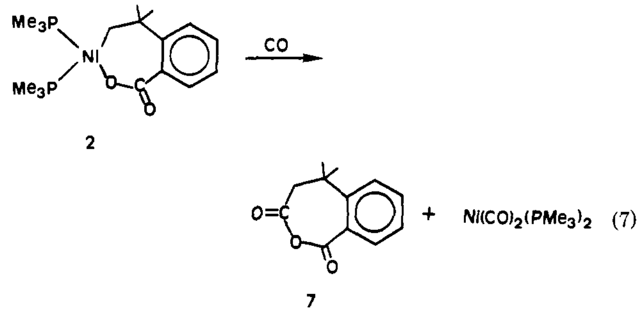
Figure 2. Molecular structure of **2** and atom-labeling scheme.

Figure 2 shows an ORTEP perspective view of the molecule of **2**; other pertinent structural data are collected in Tables I and III. As found for **1**, the coordination around nickel is distorted square planar, and there is also some tetrahedral deviation [O(1)–Ni–P(2) and P(1)–Ni–C(9) angles of 162.6 (3) and 169.3 (5)°, respectively]. The Ni–C(9) bond distance at 1.96 (1) Å is identical with the corresponding length in the original nickelacyclopentene. The Ni–O separation at 1.877 (9) Å is unexceptional.[29b,c,30] The main difference in the coordination sphere of the Ni(II) centers of compounds **1** and **2** lies in the coordination of the phosphine ligands, which is fairly unsymmetrical in **2**. While in **1** the Ni–P bonds in trans with respect to the C(alkyl) and C(aryl) bonds have almost equal bond lengths [2.192 (4) and 2.194 (4) Å, respectively], there is a large difference in **2**, in which the Ni–P(1) (trans to the Ni–C bond) separation of 2.291 (4) Å is appreciably longer than the Ni–P(2) (trans to Ni–O) distance of 2.143 (4) Å. This probably reflects the higher trans influence of the alkyl group, as compared with the carboxylate ligand.[31]

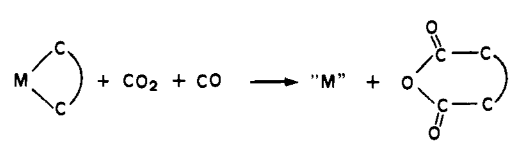
Other six-[32] and seven-membered[33] metalacyclic units are known to undergo ring contraction with formation of smaller cycles. Not unexpectedly, complex **2** does not exhibit this type of transformation and this is doubtless due to the presence of the two methyl substituents at the β-carbon. The above observation is in accord with the recent proposal by Yamamoto and co-workers[32] that ring contraction proceeds through the β-elimination process.

A final comment of interest with respect to the formation of **2** refers to the insertion mode of carbon dioxide. Although the molecular complexity found for **2** from spectroscopy and X-ray studies indicates that the insertion occurs into the Ni–C(aryl) bond, the question arises as to whether complex **2**, which is likely the thermodynamic product of the insertion, is also the kinetic product. At this respect we note that (i) carbon dioxide insertions are often reversible[21] even when the CO_2 molecule has become incorporated into a metalacyclic unit[27a,29b] and (ii), as already pointed out, the reaction of **1** with CO_2 requires 4–5 days for completion. Recent in-depth studies by Darensbourg and co-workers[21] concerning the insertion of CO_2 into the W–C bonds of the anionic alkyl or aryl derivatives, *cis*-$W(R)L(CO)_4^-$, show that the carboxylation of alkyls is faster than that of aryls, although the variation is rather small (relative rates of 1.0:3.8:6.0 have been found for R = C_6H_5:C_2H_5:CH_3). Direct unequivocal evidence on the mode of insertion has proved unattainable and therefore we will delay a definite proposal until more data are available. At present we would only like to point out that (i) CO_2 readily inserts at −78 °C into the nickel–aryl bond of the metalacycle $(Bu^n{}_3P)_2\overline{Ni(CH_2\text{-}o\text{-}C_6H_4)}$[28] and (ii) other heterocumulenes like CS_2, COS, and PhNCS insert rapidly and exclusively[23] into the nickel–aryl bond of **1**.

Complex **2** reacts rapidly with CO with formation of the cyclic anhydride **7** and $Ni(CO)_2(PMe_3)_2$, eq 7. The propensity of the



Ni–C(alkyl) bond to undergo CO insertion is doubtless responsible for the anhydride formation. The reaction proceeds likely through a cyclic acyl carboxylate intermediate. Acyclic compounds of this type are known[34] but have trans acyl and carboxylate groups and are therefore stable toward reductive elimination, in the absence of added ligands (CO). The cis arrangement of the acyl and carboxylate groups in the proposed intermediate accounts for the observed rapid reductive elimination to anhydride **7**. The transformation represented in eq 7 corresponds to a metal-mediated coupling of an organic fragment with CO_2 and CO (eq 8) to give an anhydride functionality.[29a,b]



(8)

(d) Insertion of Formaldehyde. The reaction of formaldehyde with transition-metal complexes and, in particular, its insertion into M–L bonds is receiving increasing attention in view of the intermediary role played by this molecule in CO reduction.[35] Insertions of CH_2O into M–H[36] and M–C[37] bonds are known, although they can still be considered rather uncommon reactions. Compound **1** reacts with aqueous formaldehyde, or preferably with polymeric paraformaldehyde, with formation of yellow, microcrystalline **3** in high yields. ^{31}P NMR studies show the reaction occurs with liberation of one molecule of PMe_3 per nickel atom, while analytical and molecular weight determinations reveal **3** is a binuclear species that has incorporated one molecule of CH_2O per metalacyclic unit. Compound **3** reacts with dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$) with formation of a monomeric species **4**. At this point, it is worth considering the four structural possibilities for these complexes, which derive from the two modes of insertion of CH_2O into either the Ni-alkyl or the Ni-aryl bonds. This is best accomplished with reference to the dmpe complex **4**, structures I–IV. As shown below, spectroscopic data are only consistent with structure I. The expected polarity of the nickel–carbon bonds in cyclometalated **1**, $Ni^{\delta+}$–$C^{\delta-}$, argues in principle against insertion modes III and IV. A characteristic feature in the ^{13}C NMR spectra of **4** is the observation of a strong coupling of ca. 88 Hz between the quaternary aromatic carbon atom and one of the phosphorus nuclei. This rules out structures II and IV. Also characteristic is the absence of coupling between the methylenic carbon and hydrogen atoms and the ^{31}P nuclei, and on this basis, structures II–IV may be discarded. Additional evidence for

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(30) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: London, 1983.

(31) Henrici-Olivé, G.; Olive, S. *Coordination and Catalysis, Monographs in Modern Chemistry*; Ebel, H. F., Ed.; Verlag Chemie: New York, 1977; Vol. 9, p 140.

(32) Yamamoto, T.; Sano, K.; Yamamoto, A. *J. Am. Chem. Soc.* **1987**, *109*, 1092.

(33) Hoberg, H.; Hernández, E. *J. Chem. Soc., Chem. Commun.* **1986**, 544.

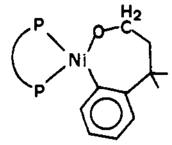
(34) Komiya, S.; Yamamoto, A.; Yamamoto, T. *Chem. Lett.* **1981**, 193.

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

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

(37) (a) Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1983**, *255*, C31. (b) Tikkanen, W. R.; Petersen, J. L. *Organometallics* **1984**, *3*, 1651.

(38) For a similar stereochemical situation, see: Glaser, R.; Kountz, D. J.; Waid, R. D.; Gallucci, J. C.; Meek, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 6324.



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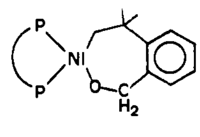
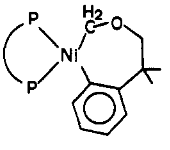
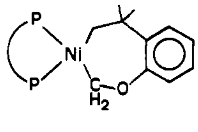


II

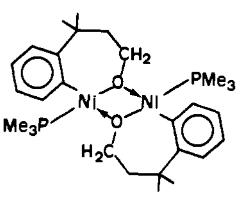


III



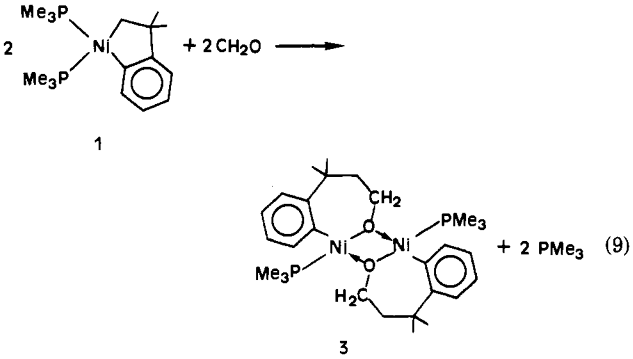
IV

structure I comes from data in the Experimental Section, and from the results of the reaction of **3** with carbon monoxide (see below). On the basis of the above considerations and the available data, structure V can be proposed for complex **3** and its formation, and



V

that of **4**, represented as in eq 9 and 10. As expected, NMR



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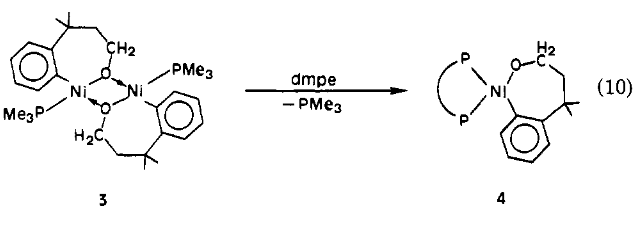
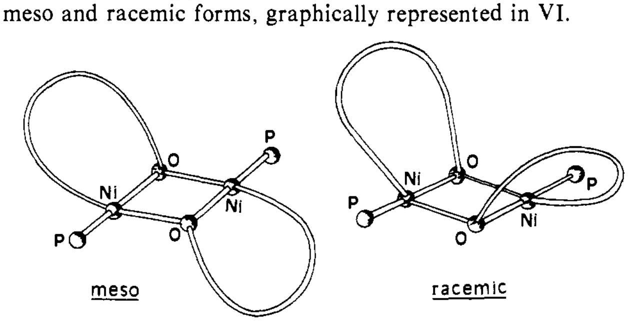


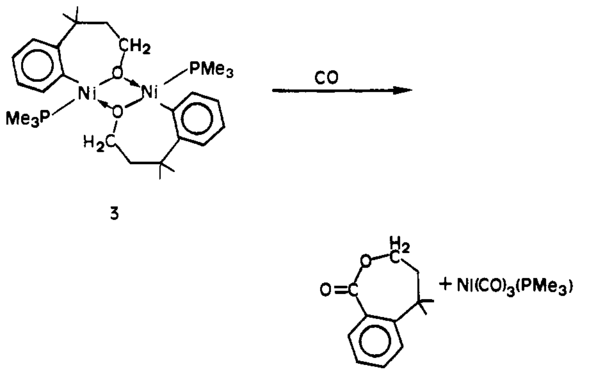
(10)

studies of solutions of complex **3** reveal the presence of two species. These are in an approximate ratio of 2:1, and correspond to the meso and racemic forms, graphically represented in VI.



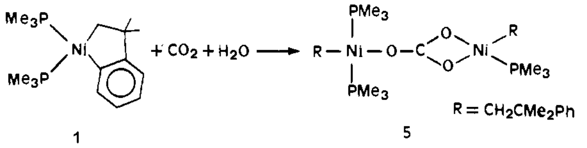
VI

Compound **3** reacts with carbon monoxide, under ambient conditions, with formation of $Ni(CO)_3(PMe_3)$, together with lactone **8** (eq 11). The reaction proceeds presumably by insertion of carbon monoxide into the Ni–C(aryl) bond,[39,40] followed by reductive elimination.



(11)

(e) The Reaction of 1 with CO_2 in the Presence of Water. When the reaction of metalacycle **1** with CO_2 is carried out with commercial, high purity (≥99.998%) carbon dioxide that has not been carefully dried, a different compound **5** is formed along with the already described nickelalactone **2**. Compound **5** is rapidly (10–15 min) and quantitatively formed when a few drops of water are added to the reaction system and can be isolated in the form of yellow crystals. The existence of a strong IR absorption at ca. 1500 cm^{-1} and of a ^{13}C resonance at 170.3 ppm implies the presence of a carbonate ligand. Analytical and molecular weight determinations indicate a binuclear nature for the complex, whose formation can be represented as in eq 12. Since cyclometalated



(12)

1 is stable toward water and, on the other hand, it reacts only very slowly with anhydrous carbon dioxide (see above), it is reasonable to assume that the active species in this reaction is carbonic acid, H_2CO_3. Attack on **1** can produce Ni–C(aryl) heterolysis with formation of an intermediate hydrogencarbonate neophyl species, $(Me_3P)_2Ni(CH_2CMe_2Ph)(HCO_3)$,[41] which by reaction with another molecule of **1** would afford the observed binuclear carbonate **5**. There is ample evidence in the literature[42] for partial protonation of dialkyl derivatives, and there is also precedent[43] for structures of the type found for **5**. A synthetic route to this class of compounds has been developed recently in our laboratory and the structure of one such derivative, $(Me_3P)_2(Me_3SiCH_2)Ni(\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3)Ni(CH_2SiMe_3)(PMe_3)$, solved by single-crystal X-ray structural analysis.[44]

Compound **5** is fluxional in solution even at temperatures down to −70 °C. The room temperature $^{31}P\{^1H\}$ NMR spectrum shows two very broad features which convert into two somewhat broad singlets (ca. 1:2 ratio) in the −70 °C spectrum. On the other hand, only one set of resonances can be seen for the neophyl groups in

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[39] CO insertion into the Ni–O bond, as observed recently in the platinum complex $Pt(CH_3)(OCH_3)(dppe)$ cannot be completely ruled out. See: Bryndza, H. E. *Organometallics* **1985**, *4*, 1686.

[40] Some acyl(aryloxy) nickel(II) complexes, similar to the proposed aroyl(alkoxy) nickel(II) intermediate have been prepared and are known to undergo reductive elimination induced by π-acids. See: Komiya, S.; Akai, Y.; Tamaka, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1985**, *4*, 1130.

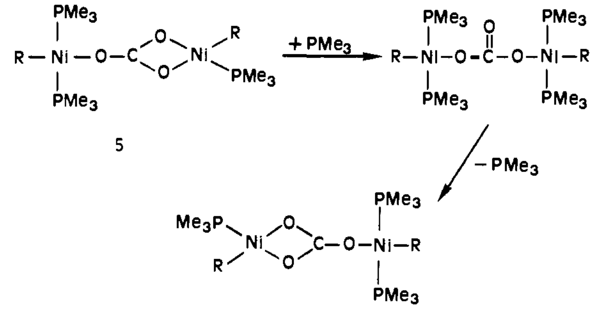
[41] The reaction of $PdMe_2(PMe_3)_2$ with CO_2 and H_2O affords the η^1-bicarbonate compound *trans*-$PdMe(O_2COH)(PMe_3)_2$. See: Crutchley, R. J.; Powell, J.; Faggiani, R.; Lock, C. J. L. *Inorg. Chim. Acta* **1977**, *24*, L15.

[42] (a) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1973**, *106*, 1433. (b) Yamamoto, T.; Kohara, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1720.

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

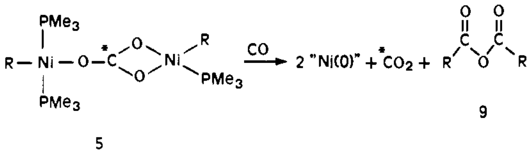
[44] Palma, P. Ph.D. Dissertation, University of Sevilla, 1986.

Scheme II



the room-temperature ^1H and ^{13}C NMR spectra. Resonances due to the methylene proton and carbon atoms are hidden into the base line, but emerge into singlets upon heating or upon addition of PMe_3. The above observations may be accounted for in terms of a very fast intermolecular phosphine exchanging process between coordinated and traces of free PMe_3, through the intermediacy of a symmetrical species containing a μ_2-η^1,η^1-CO_3 ligand, as shown in Scheme II. A similar process has been proposed by Ibers and Otsuka in a rhodium system.[45]

Rather unexpectedly, the carbonate **5** reacts with CO with reductive elimination to $Ni(CO)_n(PMe_3)_{4-n}$ (n = 2, 3) and anhydride **9**. Carbon dioxide is also produced, eq 13. Isotopic labeling studies using complex **5** enriched in ^{13}C in the carbonate ligand clearly demonstrate that the evolved CO_2[46] derives exclusively from the carbonate ligand. In a formal sense, eq 13 represents a metal-promoted oxidative conproportionation of carbonate and carbonyl ligands, $CO_3^{2-} + CO - 2e = 2CO_2$, to two molecules of carbon dioxide. To our knowledge, eq 13 constitutes the first example of a CO_3^{2-} and CO conproportionation reaction induced by a transition-metal complex. A somewhat related reaction has been reported recently[47] between allylic carbonates and carbon monoxide, in the presence of palladium catalysts. For instance, the Pd-catalyzed reaction (eq 14) of allyl ethyl carbonate with carbon monoxide produces ethyl 3-butenoate in high yield. Here again, and always in a formal sense, a carbonate group and a molecule of carbon monoxide conproportionate to two molecules of carbon dioxide. In both reactions 13 and 14, one of the molecules is evolved as free CO_2, while the other becomes incorporated into the anhydride, or ester, functionality. If reactions 12 and 13 are simultaneously considered, the overall process can be seen to correspond to a CO_2-mediated hydrocarbonylation of **1** to produce anhydride **9**, as depicted in eq 15.



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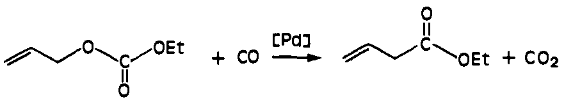
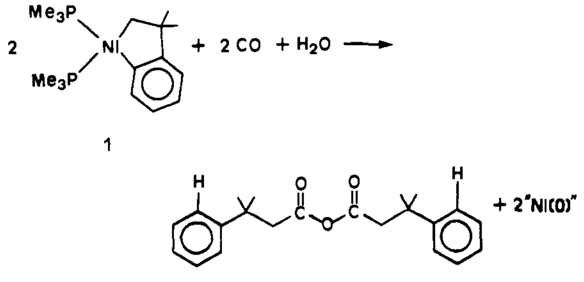


(14)



(15)

Concluding Remarks

Cyclometalated **1** exhibits a very high propensity to undergo insertion reactions. Its ready availability in a several-gram scale provides the opportunity to investigate the preferential capability of Ni–alkyl and Ni–aryl bonds toward the insertion of small, unsaturated molecules. While it proves difficult to ascertain the place of insertion of PhC≡CPh into the Ni–C bonds of **1**, formation of an acyl, as opposed to an aroyl, is kinetically favored for carbon monoxide. Formaldehyde also inserts into the Ni–C(alkyl) bond, but for CO_2 (and other heterocumulenes[23]) the insertion into the Ni–C(aryl) bond seems to be kinetically and thermodynamically favored.

Some of the reactions described in this paper have potential synthetic utility. In particular, the facile formation of the dihydronaphthalene **6** reported in this paper becomes important in view of the dearth of synthetic methods leading to such molecules. Extension of this insertion chemistry to other unsaturated molecules such as RNC, RCN, RN=C=NR, RNCS, CS_2, etc. may provide easy access to various heterocycles that are difficult to prepare by other methods.

Experimental Section

Microanalyses were by Pascher, Microanalytical Laboratory, Bonn. The spectroscopic instruments were Perkin-Elmer Models 577 and 684 for IR spectra and Varian XL-200 for NMR. The ^{13}C resonance of the solvent was used as internal standard, but chemical shifts are reported with respect to $SiMe_4$. ^{31}P NMR shifts are referenced to external 85% H_3PO_4. All preparations and other operations were carried out under oxygen-free nitrogen, following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point of 40–60 °C. PMe_3[48] and $NiCl_2(PMe_3)_2$[49] were prepared according to literature methods.

Synthesis of $(Me_3P)_2\overline{Ni(CH_2CMe_2\text{-}o\text{-}C}_6H_4)$ (1). To a stirred suspension of $NiCl_2(PMe_3)_2$ (4.45 g, ca. 16 mmol) in diethyl ether (150 mL), cooled at −50 °C, was added 25.6 mL of a ca. 1.25 N solution of $Mg(CH_2CMe_2Ph)Cl$ in diethyl ether solution. (The Grignard solution contained small amounts of MgI_2, resulting from the activation of the Mg used by I_2). The mixture was stirred at this temperature for 30 min and then at room temperature for 4 h. The solvent was removed in vacuo and the residue extracted with 180 mL of light petroleum. The suspension was centrifuged and the reddish solution obtained concentrated and cooled at −20 °C overnight. Orange prisms of the title compound were collected. Further concentration of the mother liquors and cooling at −20 °C yielded another crop of the metalacycle: total yield, 60–75%; ^1H NMR (200 MHz, C_6D_6, 20 °C) δ 0.96 (br d, 18 H, PMe_3, $J_{HPapp} = 6.3$ Hz), 1.83 (s, 2 H, $NiCH_2$), 1.89 (s, 6 H, CMe_2), 7.30–7.60 (m, 4 H, C_6H_4); $^{31}P\{^1H\}$ NMR (THF–CD_3COCD_3, −70 °C) δ −5.1 and −11.4 (s, P_A and P_B); $^{13}C\{^1H\}$ NMR (THF, CD_3COCD_3, −70 °C) δ 14.9 (d, PMe_3, $^1J_{CP} = 22$ Hz), 17.4 (d, PMe_3, $^1J_{CP} = 20$ Hz), 35.1 (s, CMe_2), 51.0 (d, CMe_2, $^3J_{CP} = 9$ Hz), 52.4 (d, $NiCH_2$, $^2J_{CP} = 16$ Hz), 120.0, 121.9, 122.5, 138.4 (s, aromatic CH carbons), 170.8 (s, aromatic quaternary carbon), 171.6 (d, NiC_{arom}, $^2J_{CP} = 79$ Hz); $^{13}C\{^1H\}$ NMR (THF–CD_3COCD_3, 20 °C) δ 16.6 (br s, PMe_3), 34.8 (s, CMe_2), 50.9 (s, CMe_2), 52.4 (s, $NiCH_2$), 120.0, 121.9, 122.4, 138.2 (s, aromatic CH carbons), 166.9 (s, aromatic quaternary carbon), 170.5 (br s, NiC_{arom}); M_w (cryoscopically, C_6H_6, N_2) calcd for $C_{16}H_{30}P_2Ni$ 343, found 323. Anal. Calcd for $C_{16}H_{30}P_2Ni$: C, 56.0; H, 8.7. Found: C, 56.2; H, 8.7.

Reaction of 1 with CO. Carbon monoxide was bubbled, at room temperature and pressure, through a solution of **1** (0.34 g, 1 mmol) in Et_2O (10 mL) for ~5 min. The resulting pale yellow solution was evaporated to dryness to furnish an almost colorless oil, which was shown by IR and ^1H, ^{13}C, and ^{31}P NMR studies to consist of a mixture of $Ni(CO)_2(PMe_3)_2$ and $\overline{CH_2CMe_2\text{-}o\text{-}C_6H_4C}{=}O$. The reaction is quantitative by NMR. $\overline{CH_2CMe_2\text{-}o\text{-}C_6H_4C}{=}O$ (**10**): ^1H NMR (200 MHz, C_6D_6) δ 1.00 (s, 6 H, CMe_2), 2.28 (s, 2H, CH_2), 6.95–7.07, 7.16–7.24, 7.73–7.78 (m, 2, 1, 1 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 21.7 (CMe_2), 29.4 (CMe_2), 73.5 (CH_2), 123.1, 123.3, 127.2, 134.3 (CH aro-

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matics), 135.8 ($C_{arom}CO$), 163.1 (C_{arom}), 203.6 (CO); IR, $\nu(C{=}O)$ at 1700 cm^{-1}.

Reaction of 1 with PhC≡CPh. (a) A mixture of **1** (0.34 g, 1 mmol) and PhC≡CPh (0.33 g, 2 mmol) was dissolved in Et_2O (40 mL) and stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure and the residue extracted with petroleum ether. The red solution obtained was concentrated to ca. 10 mL and cooled at −20 °C for 2 days, after which time a small amount of the starting material crystallized off, together with a crystalline yellow product that was separated by hand and identified as the alkyne complex $(Me_3P)_2Ni(PhC{\equiv}CPh)$ by comparison of its IR and NMR spectra (^1H, ^{13}C, and ^{31}P) with those reported in the literature.[25]

The mother liquor was concentrated to ca. 1 mL and cooled at −80 °C to provide colorless crystals (80% yield) of an organic product identified as $CH_2CMe_2\text{-}o\text{-}C_6H_4C(Ph){=}C(Ph)$.

(b) To a solution of **1** (0.34 g, 1 mmol) and PPh_3 (0.52 g, 2 mmol) in 30 mL of Et_2O, at −70 °C, was added 1 mmol of PhC≡CPh. After being stirred for 3 h at room temperature, the mixture was evaporated to dryness and the resulting oil broken up with 20 mL of MeOH. The supernatant was separated from the orange precipitate of $Ni(PMe_3)_2(PPh_3)_2$ and taken to dryness. Crystallization from petroleum ether furnished the colorless dihydronaphthalene **6** in 70% yield. $CH_2CMe_2\text{-}o\text{-}C_6H_4C(Ph){=}C(Ph)$ (**6**): ^1H NMR (200 MHz, $CDCl_3$) δ 1.50 (s, 6 H, CMe_2), 2.81 (s, 2 H, CH_2), 7.09–7.49 (m, 14 H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 28.0 (CMe_2), 34.1 (CMe_2), 45.8 (CH_2), 123.3, 125.6, 126.0, 126.9, 127.5, 127.7, 128.0, 131.1 (CH aromatics), 135.1, 135.5, 135.8, 139.8, 143.3, 144.2 (C aromatics and $C{=}C$). Anal. Calcd for $C_{24}H_{22}$: C, 92.9; H, 7.1. Found: C, 93.1; H, 7.1.

Reaction of 1 with Anhydrous CO_2. An ampule that contained a frozen solution of 0.36 g of **1** (ca. 1.05 mmol) in 10 mL of Et_2O, under vacuo, was pressurized with 2 atm of CO_2 that had been carefully dried by stirring in a Fischer–Porter pressure bottle for two periods of 3–4 days, in the presence of P_2O_5. The solution was stirred for 4 days, during which time precipitation of a yellow microcrystalline solid was observed. Cooling at −40 °C for 4–6 h and filtration provided 0.27 g of the insertion product **2**: yield, 70%; ^1H NMR (200 MHz, C_6D_6, 20 °C) δ 0.67 (d, 18 H, PMe_3, $^2J_{PH}$ = 7 Hz), 1.50 (br s, 2 H, $NiCH_2$), 1.57 (s, 6 H, CMe_2), 7.15–8.20 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C), δ −12.6 (br s); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 14.5 (d, PMe_3, $^1J_{CP}$ = 24 Hz), 34.3 (s, CMe_2), 37.6 (br s, $NiCH_2$), 39.3 (s, CMe_2), 124.1, 125.0, 128.2, 129.5 (s, CH aromatics), 142.9, 149.3 (br s and s, quaternary aromatics), 175.5 (s, $NiOC(O)$); IR (Nujol mull) $\nu(COO)$ at 1610 cm^{-1}. Anal. Calcd for $C_{17}H_{30}P_2O_2Ni$: C, 52.7; H, 7.8. Found: C, 52.5; H, 7.8.

Reaction of 1 with CO_2 and Water. A 0.96-g (ca. 2.8 mmol) portion of **1** was dissolved in 25 mL of Et_2O to which 0.1 mL of water had been added. The flask was filled with commercial CO_2 and the solution stirred at room temperature for 1 h. Partial evaporation of the solvent and cooling at −30 °C overnight furnished the dimetallic carbonate **5** in almost quantitative yield. $(Me_3P)_2(PhCMe_2CH_2)Ni(\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3)Ni(CH_2CMe_2Ph)(PMe_3)$ (**5**): ^1H NMR (200 MHz, C_6D_6, 20 °C) δ 0.57 (br s, 4 H, $NiCH_2$), 0.86 (br s, 27 H, PMe_3), 1.87 (s, 12 H, CMe_2), 7.12–8.21 (m, 10 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C) δ −17.3 (br s, 2 P_A), −3.8 (br s, P_B); $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C) δ 12.3 (br s, PMe_3), 18.0 (v br, $NiCH_2$), 32.5 (s, CMe_2), 41.0 (s, CMe_2), 124.6, 126.5, 127.7 (s, CH aromatics), 154.1 (br s, quaternary aromatic carbon), 170.4 (s, CO_3); 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.

Reaction of $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4C(O)O)$ (2) with CO. Through a solution of **2** in Et_2O was bubbled CO at room temperature for ca. 5 min. The pale yellow solution formed was evaporated to dryness and the residue extracted with petroleum ether and cooled at −70 °C to yield the organic anhydride $CH_2CMe_2\text{-}o\text{-}C_6H_4C(O)OC(O)$ (**7**) as colorless crystals. NMR studies carried out with the mother liquor revealed the presence of $Ni(CO)_2(PMe_3)_2$. The organic anhydride was identified by microanalyses, IR, ^1H and ^{13}C NMR and mass spectroscopies, and by conversion to the diacid $HOOCCH_2CMe_2\text{-}o\text{-}C_6H_4COOH$, isolated by alkaline hydrolysis, acidification, and extraction with petroleum ether. $CH_2CMe_2\text{-}o\text{-}C_6H_4C(O)OC(O)$ (**7**): ^1H NMR (200 MHz, $CDCl_3$) δ 1.44 (s, 6 H, CMe_2), 2.88 (s, 2 H, CH_2), 7.50–7.56 (m, 4 H, aromatics); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.3 (CMe_2), 37.1 (CMe_2), 47.7 (CH_2), 127.2, 127.8, 133.1, 133.4 (CH aromatics), 147.0 (quaternary aromatic), 164.4 and 165.3 ($C(O)OC(O)$); IR (Nujol mull) $\nu(CO)$ at 1730 and 1790 cm^{-1}; MS, *m/e* 204. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.6; H, 5.9. Found: C, 69.1; H, 6.1.

Reaction of $Ni_2(\mu_2\text{-}\eta^1,\eta^2\text{-}{*}CO_3)(CH_2CMe_2Ph)_2(PMe_3)_3$ with CO. A 0.18-g (0.28 mmol) portion of the title compound **5**, ^{13}C-enriched in the bridging carbonate, obtained by reaction of **1** with $^{13}CO_2$ in the presence of water, was dissolved in Et_2O (20 mL) and the solution transferred into an ampule, which was pressurized with 2 atm of CO for 4 h. The solution was then frozen by cooling with liquid nitrogen and degassed under vacuum to eliminate the unreacted CO. The resulting mixture was then warmed to room temperature, and the volatiles were collected in a vessel by trap-to-trap distillation. IR and NMR (C_6D_6) spectra of the residue allowed the identification of $Ni(CO)_2(PMe_3)_2$, $Ni(CO)_3(PMe_3)$, and the organic anhydride $(C_6H_5CMe_2CH_2CO)_2O$ (**9**) as the products of this reaction. The previously distilled volatile fraction was qualitatively analyzed by GC and ^{13}C NMR, and the amount of $*CO_2$ was precisely determined by reacting it with metalacycle **1** and water. The yield of the isolated carbonate **5** was 85%, referred to the total amount of CO_2 expected to evolve in the above reaction. $(C_6H_5CMe_2CH_2CO)_2O$ (**9**): ^1H NMR (200 MHz, C_6D_6) δ 1.21 (s, 6 H, CMe_2), 2.26 (s, 2 H, CH_2), 7.12 (m, 5 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 28.4 (CMe_2), 36.8 (CMe_2), 48.3 (CH_2), 125.5, 126.1, 128.2 (2, 1, and 2 CH aromatics), 147.5 (quaternary aromatic), 166.7 (CO); IR (Nujol mull) $\nu(CO)$ at 1750 and 1820 cm^{-1}. After hydrolysis, the isolated acid, $C_6H_5CMe_2CH_2COOH$, was shown to be identical (IR, ^1H and ^{13}C NMR) with an authentic sample obtained from $Mg(CH_2CMe_2Ph)Cl$ and CO_2.

Reaction of 1 with CH_2O. Formation of the Oxynickelacycloheptene $[(Me_3P)Ni(OCH_2CH_2CMe_2\text{-}o\text{-}C_6H_4)]_2$ (3). A mixture of **1** (1.56 g, 4.55 mmol) and excess of paraformaldehyde was stirred in THF, at room temperature, for 4 h, during which time the color of the solution changed from orange to yellow. The solvent was evaporated and the residue extracted with 80 mL of a mixture of diethyl ether–petroleum ether. Centrifugation, partial removal of the solvent, and cooling at −30 °C overnight furnished 1.15 g (85%) of the crude product. Recrystallization from Et_2O at −30 °C provided pure **3** in ca. 70% yield. Major isomer: ^1H NMR (200 MHz, C_6D_6, 20 °C) δ 0.52 (d, 9 H, PMe_3, $^2J_{HP}$ = 8.5 Hz), 1.49 and 3.16 (s, 3 H and 3 H, diastereotopic CMe_2), $OCH_AH_BCH_CH_D$ group at 1.55 (dt, 1 H, H_D, $^2J_{DC}$ = 10.4 Hz, $^3J_{DA}$ = 3.7 Hz, $^3J_{DB}$ = 3.0 Hz), 3.0 (overlap m, 1 H, H_B), 3.55 (ddd, 1 H, H_C, $^3J_{CB}$ = 11.0 Hz, $^3J_{CA}$ = 3.7 Hz), 3.70 (dq, 1 H, H_A, $^2J_{AB}$ = 11.0 Hz), 6.85–7.91 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −12.7 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 13.7 (d, PMe_3, $^1J_{CP}$ = 28 Hz), 31.6 and 35.2 (s, diastereotopic CMe_2), 37.7 (s, CMe_2), 50.4 (s, Me_2CCCH_2), 65.5 (s, OCH_2), 122.1, 122.3, 123.9 (s, CH aromatics), 135.7 (d, aromatic CH, J_{CP} = 11 Hz), 147.8 (d, aromatic carbon bound to Ni, $^2J_{CP}$ = 42 Hz), 153.3 (s, quaternary aromatic). Minor isomer: ^1H NMR (200 MHz, C_6D_6) δ 0.56 (d, 9 H, PMe_3, $^2J_{HP}$ = 7.4 Hz), 1.48 and 3.13 (s, 3 H and 3 H, diastereotopic CMe_2), the OCH_2CH_2 and aromatic protons not assigned; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −7.0 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 13.4 (d, PMe_3, $^1J_{CP}$ = 28 Hz), 32.1 and 33.2 (s, diastereotopic CMe_2), 37.3 (s, CMe_2), 49.9 (s, Me_2CCH_2), 66.3 (s, OCH_2), 122.2, 122.4, 122.9 (s, CH aromatics), 136.7 (d, aromatic CH, J_{CP} = 10 Hz), 149.8 (d, aromatic carbon bound to Ni, $^2J_{CP}$ = 40 Hz), 154.9 (s, quaternary aromatic). M_w (cryscopically, C_6H_6, N_2) 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.

Reaction of $[(Me_3P)Ni(OCH_2CH_2CMe_2\text{-}o\text{-}C_6H_4)]_2$ (3) with CO. A 0.1-g (0.16 mmol) portion of complex **3** was dissolved in 0.5 mL of C_6D_6 and the solution transferred to a small ampule, which was pressurized with 2 atm of CO for ca. 30 min. The resulting solution was transferred to a NMR tube and shown by ^1H, ^{31}P, and ^{13}C NMR studies to contain $OCH_2CH_2CMe_2\text{-}o\text{-}C_6H_4C{=}O$ and $Ni(CO)_3(PMe_3)$ as the reaction products. $OCH_2CH_2CMe_2\text{-}o\text{-}C_6H_4C{=}O$ (**8**): ^1H NMR (200 MHz, C_6D_6) δ 1.06 (s, 6 H, CMe_2), 1.37 (t, 2 H, Me_2CCH_2, $^3J_{HH}$ = 5.8 Hz), 3.56 (t, 2 H, OCH_2), 7.00–7.80 (m, 4 H, aromatics); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 31.5 (CMe_2), 42.2 (Me_2CCH_2), 66.4 ($O\text{-}CH_2$), 124.7, 126.9, 131.4, 131.7 (CH aromatics), 172.0 (COO).

Reaction of 3 with dmpe. Formation of $(dmpe)Ni(OCH_2CH_2CMe_2\text{-}o\text{-}C_6H_4)$ (4). To a solution of 0.47 g of the dimer **3** (0.8 mmol) in 40 mL of Et_2O was added dmpe (0.32 mL, ca. 1.6 mmol). The mixture was stirred at room temperature for 2 h, with occasional pumping to remove the PMe_3 produced in the reaction. The solvent was then stripped off in vacuo and the residue extracted with Et_2O and centrifuged. After concentration and cooling at −30 °C overnight, the desired complex **4** was obtained in almost quantitative yield: ^1H NMR (200 MHz, C_6D_6) δ 0.44 (d, 3 H, PMe_A, $^2J_{HP}$ = 9.9 Hz), 0.87 (d, 3 H, PMe_B, $^2J_{HP}$ = 8.8 Hz), 1.18 (d, 3 H, PMe_C, $^2J_{HP}$ = 8.7 Hz), 1.20 (d, 3 H, PMe_D, $^2J_{HP}$ = 8.8 Hz), 0.5–1.5 (complex m, PCH_2CH_2P group), 1.57 and 2.94 (s, 3 H and 3 H, diastereotopic CMe_2), $OCH_AH_BCH_CH_D$ group at 1.47 (br d, 1 H, H_D, $^2J_{DC}$ = 13.6 Hz), 2.15 (td, 1 H, H_C, $^3J_{CB}$ = 11.4 Hz, $^3J_{CA}$ = 4.4 Hz), 3.28 (br t, 1 H, H_B, $^2J_{BA}$ = 11.4 Hz), 3.96 (td, 1 H, H_A, $^4J_{HP}$ = 11.4 Hz), 7.06–7.74 (m, 4 H, aromatics); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 28.2 (d), 29.9 (d, J_{PP} = 19 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 10.5 (d, PMe_A, $^1J_{CP}$ = 17 Hz), 10.8 (d, PMe_B, $^1J_{CP}$ = 23 Hz), 11.8 (d, PMe_C,

$^1J_{CP}$ = 17 Hz), 11.8 (dd, PMe_D, $^1J_{CP}$ = 31 Hz, $^3J_{CP}$ = 4 Hz), 22.8 (dd, PC_AH$_2$, $^1J_{CP}$ = 26 Hz, $^2J_{CP}$ = 11 Hz), 30.2 (dd, PC_BH$_2$, $^1J_{CP}$ = 31 Hz, $^2J_{CP}$ = 23 Hz), 33.2 and 35.9 (s, diastereotopic CMe_2), 38.6 (d, *C*Me$_2$, $^4J_{CP}$ = 3 Hz), 52.2 (s, Me$_2$C*C*H$_2$), 66.8 (d, O*C*H$_2$, $^3J_{CP}$ = 8 Hz), 122.7, 122.8 (s, CH aromatics), 124.1 and 135.5 (d, CH aromatics, J_{CP} = 6 and 10 Hz respectively), 153.8 (d, quaternary aromatic, J_{CP} = 5 Hz), 166.2 (dd, aromatic C bound to Ni, $^2J_{CP}$ = 88 Hz, $^2J_{CP'}$ = 32 Hz). Anal. Calcd for $C_{17}H_{30}OP_2Ni$: C, 55.0; H, 8.1. Found: C, 53.0; H, 8.1.

X-ray Structure Determinations. A summary of the fundamental crystal data for the compounds **1** and **2** is given in Table I.

Compound 1. A yellow crystal of irregular shape was epoxy resin coated and mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflections with $1 < \sigma < 22$ and the (h,k,l) range from (-8, 0,0) to (8,19,12) was measured with Mo Kα radiation (λ = 0.71069 Å) and $\omega/2\theta$ scan technique. The crystal became damaged by radiation. The intensities were scaled from the variation of three standard reflections whose intensities fell to 40% at the end of the data collection. The intensities were corrected for Lorentz and polarization effects and 1439 of these were considered as observed with $I > 3\sigma(I)$. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni and P were taken from a standard reference.[50] The structure was solved by Patterson and Fourier methods. Anisotropic full-matrix least-squares refinement with unit weights, minimizing $\sum\omega(|F_o| - |F_c|)^2$ lead to R = 0.083. Final refinement with fixed isotropic temperature factors and coordinates for H atoms gave R = 0.077 and R_w = 0.090. No trend in ΔF vs F_o or sin θ/λ was observed. Most of the calculations were carried out with the X-RAY 80 system.[51]

Compound 2. A yellow prismatic crystal (0.5 × 0.3 × 0.2 mm) was sealed under nitrogen 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-hydrogen atoms except the methyl carbons attached to phosphorus (2). Unit weights were used (no trend in ΔF vs F_o or sin θ/λ was observed), and at convergence, R_F = 0.067. An absorption correction was applied.[52]

Acknowledgment. Generous support of this work by the Agencia Nacional de Evaluación y Prospectiva is very gratefully acknowledged. M.P. thanks the Ministerio de Educación y Ciencia for support of a research grant.

Registry No. 1, 104090-29-1; **2**, 104090-31-5; **3**, 104090-32-6; **4**, 118977-58-5; **5**, 104090-30-4; **6**, 118921-59-8; **7**, 104090-26-8; **8**, 104090-27-9; **9**, 104090-28-0; $NiCl_2(PMe_3)_2$, 19232-05-4; Mg-$(CH_2CMe_2Ph)Cl$, 35293-35-7; CO, 630-08-0; $\overline{CH_2CMe_2\text{-}o\text{-}C_6H_4C}{=}O$, 26465-81-6; PhC≡CPh, 501-65-5; CO_2, 124-38-9; CH_2O, 50-00-0; CS_2, 75-15-0; *trans*-Ni$(COCH_2SiMe_3)Cl(PMe_3)_2$, 75982-73-9; *trans*-Ni-$(CH_2SiMe_3)Cl(PMe_3)_2$, 75982-54-6; $O{=}\overline{CCH_2CMe_2\text{-}o\text{-}C_6H_4C(S)S}$, 118921-60-1.

Supplementary Material Available: Tables of final fractional coordinates and thermal parameters for **1** and **2** (4 pages); observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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Chemical Oscillators in Group VIA: The Cu(II)-Catalyzed Reaction between Thiosulfate and Peroxodisulfate Ions[1]

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Abstract: Sustained oscillations in redox potential, pH, and the concentration of dissolved O_2 are reported in the Cu(II)-catalyzed reaction between $K_2S_2O_8$ and $Na_2S_2O_3$ in a stirred tank reactor. A range of steady states is found, most of which can be unambiguously designated as either high or low pH, but there is no evidence of bistability. A free-radical mechanism in which Cu(I), Cu(III), and the radicals $SO_4^{\bullet-}$ and $S_2O_3^{\bullet-}$ play key roles appears to be capable of accounting both for the observed kinetics (first order in $S_2O_8^{2-}$ and Cu(II), zeroth order in $S_2O_3^{2-}$) of the batch reaction and for the oscillations in the flow system.

The past decade has witnessed a virtual explosion in the number of reactions that exhibit chemical oscillation. The first successes in the search for new chemical oscillators were confined to reactions in which oxyhalogen species played the key roles.[2] Because they allow facile redox transformations among a large number of oxidation states, the group VIIA elements are excellent candidates for generating the autocatalytic buildup or decay of transient species that has proved to be conducive to oscillation and other forms of exotic dynamical behavior.

Like the halogens, the elements of groups VA and VIA possess many stable oxidation states and easily undergo redox reactions among these states. To date, no oscillatory reactions based on nitrogen or phosphorus chemistry have been reported. However, several chemical oscillators have been found in which oxygen and/or sulfur species provide the driving force. These include the sulfide–sulfite–oxygen–methylene blue,[3] hydrogen peroxide–sulfide,[4] Cu(II)-catalyzed hydrogen peroxide–thiosulfate[5] and hydrogen peroxide–thiocyanate,[6] and the Ag(I)-catalyzed sulfide–peroxodisulfate[7] reactions. Although none of these systems has been characterized in anything like the mechanistic detail available for several of the halogen-based oscillators, it is already clear that the group VIA oscillators show a far greater range of

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