the clusters where X = NCO, Cl, and Br, the lowest temperature exchange process averages all of the equatorial sites. Involvement of the axial carbonyls in this process occurs via a series of trigonal-twist steps and/or pairwise bridge–terminal CO-exchange steps. With $[Os_3I(CO)_{11}]^-$, all of the carbonyls undergo exchange at the same temperature, possibly through a rate-limiting trigonal twist of the $OsI(CO)_2$ group.

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Registry No. $PPN[Os_3Cl(CO)_{11}]$, 119909-83-0; $PPN[Os_3Br(CO)_{11}]$, 119909-85-2; $PPN[Os_3I(CO)_{11}]$, 119909-87-4; $Os_3(CO)_{12}$, 15696-40-9; Me_3NO, 1184-78-7; $PPN[Os_3(NCO)(CO)_{11}]$, 119945-41-4; $PPN(N_3)$, 38011-36-8; CO, 630-08-0.

Supplementary Material Available: Listings of positional and thermal parameters for H atoms, temperature factors, complete bond distances and angles, and crystallographic data (26 pages); tables of calculated and observed structure factors (71 pages). Ordering information is given on any current masthead page.

Contribution from the Departamento de Química Inorgánica-Instituto de Ciencia de Materiales, Universidad de Sevilla-CSIC, 41071 Sevilla, Spain

Pyrrolyl, Hydroxo, and Carbonate Organometallic Derivatives of Nickel(II). Crystal and Molecular Structure of $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2\cdot 2,5\text{-}HNC_4H_2Me_2$

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Pyrrolyl–organometallic derivatives of Ni(II), of composition $Ni(R)(NC_4H_2X_2)(PMe_3)_2$ (X = H (**1a–5a**), 2,5-Me (**1b–5b**); R = Me (**1**), CH_2SiMe_3 (**2**), CH_2CMe_3 (**3**), CH_2CMe_2Ph (**4**), 2,4,6-$C_6H_2Me_3$ (**5**)), have been obtained by treatment of the complexes *trans*-$Ni(R)Cl(PMe_3)_2$ with the sodium salt of the pyrrolyl ligand. The action of wet CO_2 upon solutions of **2a,b** provides the carbonate $Ni_2(CH_2SiMe_3)_2(CO_3)(PMe_3)_3$ (**10**), possibly through the intermediacy of a dimeric hydroxide, $[Ni(CH_2SiMe_3)(PMe_3)(\mu\text{-}OH)]_2$ (**6**). Hydroxides related to **6**, $[Ni(R)(PMe_3)(\mu\text{-}OH)]_2$ (R = CH_2CMe_2Ph (**7**), $CH_2C_6H_5$ (**8**)), have been produced by reacting the corresponding monoalkyl chlorides with powdered NaOH and have been shown to react with CO_2 with formation of carbonates analogous to **10**, $Ni_2R_2(CO_3)(PMe_3)_3$ (R = CH_3 (**9**), CH_2SiMe_3 (**10**), $CH_2C_6H_5$ (**11**), C_6H_5 (**12**)). The hydroxides readily form solid-state adducts, when crystallized in the presence of pyrrole or 2,5-dimethylpyrrole. NMR studies show these adducts are completely dissociated in solution, but an O···H–N hydrogen-bonding interaction exists in the solid state, as revealed by the results of an X-ray structural determination, carried out with the *o*-methylbenzyl complex $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2\cdot 2,5\text{-}HNC_4H_2Me_2$. The crystals are monoclinic, space group $C2/c$, with cell dimensions a = 15.598 (6) Å, b = 12.655 (7) Å, c = 17.705 (6) Å, β = 111.72 (4)°, V = 3243.7 Å^3, and Z = 4. The structure consists of dinuclear $Ni_2(\eta^1\text{-}CH_2C_6H_4\text{-}o\text{-}Me)_2(PMe_3)_2(\mu\text{-}OH)_2$ molecules and of 2,5-dimethylpyrrole molecules of crystallization, all of them showing crystallographic 2-fold symmetry. The Ni dimers have dihedral geometry, with the Ni atoms situated in a distorted square-planar environment.

Introduction

Numerous studies have been reported concerning the carbonylation of nickel–carbon bonds.[1,2] Less well studied, although of increasing interest, is the analogous carboxylation reaction.[3] Recent work by Yamamoto and co-workers has shown that the possibility of reductive elimination at the metal center in complexes $Ni(R)XL_2$ (R = alkyl or aryl group), following carbonylation depends, among other factors, upon the strength of the Ni–X bond.[4] The same arguments apply probably to the insertion of carbon dioxide but this process is less well documented. On the other hand, the reactions of carbon dioxide with transition-metal compounds are very often complicated by the unpredictable effect of small amounts of water that accompany CO_2 and that are difficult to remove completely. This is in fact a pervasive feature of carbon dioxide chemistry and leads frequently to the formation of hydroxo or carbonate complexes.[5]

As part of continuing studies on the organometallic chemistry of nickel, we have carried out the preparation of some alkyl and aryl complexes, $NiR(NC_4H_2X_2)(PMe_3)_2$, containing the pyrrolyl group. The study of their reactions with CO and CO_2 are the subject of this paper. As discussed below, insertion of carbon monoxide is generally observed, but for carbon dioxide, formation of the binuclear carbonates, $Ni_2R_2(PMe_3)_3(\mu\text{-}CO_3)$, takes place. The latter reaction does not have general application, but a general route to carbonates of this type, through the intermediacy of hydroxo-bridged species, $[NiR(PMe_3)(\mu\text{-}OH)]_2$, has been developed.

Results and Discussion

η^1-*N*-Pyrrolyl Complexes, $Ni(R)(NC_4H_2X_2)(PMe_3)_2$ (1–5). Treatment of diethyl ether solutions of alkyl or aryl complexes of Ni(II) of composition *trans*-$Ni(R)Cl(PMe_3)_2$, with the sodium salt of pyrrole or 2,5-dimethylpyrrole, $NaNC_4H_2X_2$ (X = H, Me), provides yellow crystalline derivatives, $Ni(R)(NC_4H_2X_2)(PMe_3)_2$ (**1–5**) as shown in eq 1. Spectroscopic studies clearly indicate

$$Ni(R)Cl(PMe_3)_2 + NaNC_4H_2X_2 \rightarrow NiR(NC_4H_2X_2)(PMe_3)_2 + NaCl \quad (1)$$

a, X = H; **b**, X = Me
1, R = Me
2, R = CH_2SiMe_3
3, R = CH_2CMe_3
4, R = CH_2CMe_2Ph
5, R = 2,4,6-$C_6H_2Me_3$

that compounds **1–5** exist in solution[6] as square-planar species, with trans phosphine groups and a monohapto, N-bonded pyrrolyl ligand. They can therefore be considered as alkane- (or arene-) amide complexes of nickel.[7-10] Rather interestingly, **1b** forms

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(6) Solutions of compounds **1–5** are fairly stable to hydrolysis. This is at variance with the behavior found for $Ni(CH_2C_6H_4\text{-}o\text{-}Me)(NC_4H_2Me_2)(PMe_3)_2$, see: Carmona, E.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757.

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a solid-state adduct, $NiMe(NC_4H_2Me_2)(PMe_3)_2{\cdot}HNC_4H_2Me_2$, when crystallized in the presence of 2,5-dimethylpyrrole. NMR studies demonstrate this adduct is completely dissociated in C_6D_6 solutions, but in the solid state there is a hydrogen-bonding interaction, N–H···N, between the N–H bond of the solvating pyrrole molecule and the N atom of the coordinated pyrrolyl ligand. This proposal is substantiated by the shift to lower frequencies of ν(N–H) observed in the adduct, as compared with free 2,5-dimethylpyrrole (3350 and 3280 vs 3450 and 3340 cm^{-1}, respectively) and also by the close similarity found with the related adduct $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2{\cdot}HNC_4H_2Me_2$, for which an X-ray analysis, to be discussed below, reveals a hydrogen-bonding interaction between the OH ligands and the pyrrole N–H group.[11]

Carbonylation of alkyl complexes of Ni(II) of composition $Ni(R)YL_2$, is known to provide isolable acyl species, $Ni(COR)YL_2$, when Y is a halide, pseudohalide, or similar ligand.[12] In other cases, products resulting from reductive elimination (before or after insertion) or from other decomposition pathways may be formed.[13] Recent work by Yamamoto and co-workers has shown that if the Ni–COR and the Ni–Y bonds have similar strength, the weakening of both bonds, which is thought to precede reductive elimination, can occur in a concerted manner, giving rise to the products of the reductive elimination. Transition-metal–nitrogen bonds are generally weaker than corresponding M–O bonds,[14] and for the group 8–10 metals, M–O and M–C bonds have comparable thermodynamic stability.[15] The reactions of **1–5** with CO are therefore expected to provide the reductive-elimination products following insertion, and to confirm this the carbonylation of some representative members of this series has been carried out, with the following results: (i) a solution of **2a** in diethyl ether reacts smoothly with CO (eq 2) with formation of $Ni(CO)_2(PMe_3)_2$ and

$$Ni(CH_2SiMe_3)(NC_4H_4)(PMe_3)_2 \xrightarrow{CO} Ni(CO)_2(PMe_3)_2 + Me_3SiCH_2C(O)NC_4H_4 \quad (2)$$

the amide $Me_3SiCH_2C(O)NC_4H_4$, as the only detectable products. Therefore, the CO insertion is followed by reductive elimination. Complex **2b**, which contains the more sterically demanding and stronger electron-releasing $^-NC_4H_2Me_2$ group, reacts with CO as described above for **2a**. (ii) The more sterically crowded mesityl derivative **5a** reacts with CO in a way similar to that depicted in eq 2, but more forcing conditions are required (3 atm of CO). Not unexpectedly, the even more sterically crowded complex **5b** does not react with CO (3 atm, 4 days, 20 °C). The well-known ortho effect may be invoked to account for these observations.[16]

In concluding this section, it can be noted that while the alkyl- (or aryl-) pyrrolyl complexes of Ni(II) investigated in this work are thermally stable species, their acyl counterparts are not under the conditions studied and rearrange to the reductive-elimination products. The decrease in the strength of the Ni–C bond in the order Ni–C(alkyl) > Ni–C(acyl)[17] may have some influence in this transformation but the well-known propensity of CO and other neutral ligands to induce reductive elimination in complexes of this type[18] should also be taken into account.

Reactions of the Pyrrolyl Compounds $NiR(NC_4H_2X_2)(PMe_3)_2$ with CO_2 and H_2O. Hydroxo- and Carbonate-Bridged Complexes. As mentioned above, the pyrrolyl complexes **1–5** seem to be stable to the action of water. This markedly contrasts with the rapid hydrolysis undergone by the *o*-methylbenzyl derivative $Ni(CH_2C_6H_4\text{-}o\text{-}Me)(NC_4H_2Me_2)(PMe_3)_2$, which affords[6] the dimeric hydroxo-bridged species $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2$. It is possible that an acid–base hydrolytic equilibrium (eq 3) is set up for these pyrrolyl complexes, and that this

$$2NiR(NC_4H_2X_2)(PMe_3)_2 + 2H_2O \rightleftharpoons [NiR(PMe_3)(\mu\text{-}OH)]_2 + 2HNC_4H_2X_2 + 2PMe_3 \quad (3)$$

equilibrium lies well to the left for compounds **1–5**, but far to the right for the *o*-methylbenzyl complex.

To further investigate the chemical properties of the pyrrolyls **1–5**, their reactivity toward CO_2 has been studied. Compounds **2a,b** react with commercial CO_2 (3 atm, 20 °C) with production of the red crystalline species **10**. Analytical, IR, and NMR data (see below) argue against formulation of **10** as a carboxylate complex, i.e., the product of the insertion of CO_2 into the Ni–C bond of **2a,b**, and suggest instead the existence of a carbonate ligand bridging two nickel centers, $Ni_2R_2(PMe_3)_3(\mu\text{-}CO_3)$. If very carefully dried CO_2 is used for the reaction, formation of compound **10** is not observed. On the other hand, the reaction does not have general applicability, and for example, compounds **3a,b** fail to yield the analogous carbonate complex under the same conditions. Two mechanistic pathways can be envisaged to account for the formation of the carbonate. (i) The first is protolytic cleavage of the Ni–N bond in compounds **1–5** by action of carbonic acid, H_2CO_3. This would produce initially a bicarbonate intermediate species, $NiR(O_2COH)(PMe_3)_2$,[19] which by reaction with another molecule of the pyrrolyl complex would afford the observed carbonates. (ii) The second is direct action of CO_2 (or H_2CO_3) upon the equilibrium concentration of the hydroxo dimers, $[NiR(PMe_3)(\mu\text{-}OH)]_2$, of eq 3. No clear distinction between these alternatives can be achieved, but failure to generalize formation of the carbonate complexes by the reaction of CO_2 and water with complexes **1–5**, i.e., by route i, and the successful exploitation of route ii, that is, reaction of CO_2 with $[NiR(PMe_3)(\mu\text{-}OH)]_2$ complexes (see below), seem more in favor of the latter. Since a general synthesis of the carbonates $Ni_2R_2(PMe_3)_3(\mu\text{-}CO_3)$, implicates the hydroxo species $[NiR(PMe_3)(\mu\text{-}OH)]_2$, these will be discussed first.

(a) Hydroxo-Bridged Complexes $[NiR(PMe_3)(\mu\text{-}OH)]_2$. Crystal and Molecular Structure of the Solid-State Adduct $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2{\cdot}HNC_4H_2Me_2$. The first alkylnickel dimer containing bridging hydroxo ligands, $[NiMe(PMe_3)(\mu\text{-}OH)]_2$, was reported by Klein and Karsch[20] in 1973. Related compounds have now been prepared by the same procedure, namely by treatment of the monoalkyls *trans*-$Ni(R)X(PMe_3)_2$ with powdered NaOH in tetrahydrofuran or diethyl ether solutions (eq 4). Compounds **6–8** have been obtained as yellow

$$2Ni(R)Cl(PMe_3)_2 + 2NaOH \rightarrow [NiR(PMe_3)(\mu\text{-}OH)]_2 + 2PMe_3 + 2NaCl \quad (4)$$

6, R = CH_2SiMe_3
7, R = CH_2CMe_2Ph
8, R = $CH_2C_6H_5$

crystalline solids that exhibit high solubility in common organic solvents. The presence of a hydroxo ligand is manifested by the

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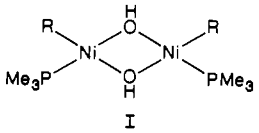
Table I. ^{1}H, ^{31}P, and ^{13}C NMR Data (δ; J in Hz) for Complexes **6–12**

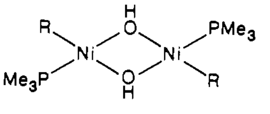
	PMe$_3$			^{1}H			^{13}C{^{1}H}		
	^{1}H ($^{2}J_{HP}$)	^{13}C{^{1}H} ($^{1}J_{CP}$)	^{31}P{^{1}H}	OH	CH$_2$ ($^{3}J_{HP}$)	CH$_3$	CH$_2$ ($^{2}J_{CP}$)	CH$_3$	CO$_3$
cis-**6**	0.65 d (9.1)	13.0 d (27.4)	−8.2 s	−6.51 s −2.80 s	−1.32 d (9.6)	0.52 s	−14.7 d (29.8)	0.5 s	
trans-**6**	0.60 d (8.8)	13.2 d (29.1)	−9.5 s	−4.63 s	−1.52 d (9.4)	0.50 s	−14.5 d (32.1)	3.5 s	
cis-**7**[a]	0.47 d (9.0)	12.6 d (23.1)	−7.5 s	−6.59 s −2.41 s	0.24 d (8.9)	1.56 s	17.6 d (32.3)	33.1 s	
trans-**7**[b]	0.41 d (8.7)	12.6 d (31.7)	−8.5 s	−4.56 s	0.15 d (8.8)	1.56 s	16.8 d (34.5)	33.7 s	
8[c]	0.46 d (7.2)	12.1 d (27.1)	−7.8 s	−4.80 s	0.81 d (6.0)		6.8 br s		
9	0.86 d (8.4)	12.2 d (24.8)	−10.7 br s			0.76 s		−20.2 s	170.8 s
10	1.06 br s	12.7 br s	−16.1 br s		−1.06 br s	0.53 br s	−16.2 br s	3.4 s	170.7 s
11[d]	0.80 br s	12.0 d (14.6)	−12.3 br s		1.55 br s		4.9 br s		170.2 s
12[e]	0.74 br s	12.0 br s	−12.0 br s						170.4 s

[a] δ 6.9–8.1 (m, CH_{arom}), 40.1 (s, *C*Me), 124.6, 126.5, and 127.6 (s, 1, 2, and 2 *C*H$_{arom}$), 153.9 (s, quat arom *C*). [b] δ 6.9–8.0 (m, CH_{arom}), 40.0 (s, *C*Me), 124.6, 126.5, and 127.6 (s, 1, 2, and 2 *C*H$_{arom}$), 153.8 (s, quat arom *C*). [c] δ 6.8–7.5 (m, CH_{arom}), 121.5, 127.7, and 128.1 (s, 1, 2, and 2 *C*H$_{arom}$), 151.8 (s, quat arom *C*). [d] δ 7.1–7.9 (m, CH_{arom}), 123.0, 128.0, and 129.1 (s, 1, 2, and 2 *C*H$_{arom}$), 148.9 (s, quat arom *C*). [e] δ 6.7–7.0 (m, CH_{arom}), 121.8, 125.8, and 137.1 (s, 1, 2, and 2 *C*H$_{arom}$), 150.6 (s, quat arom *C*).

observation of characteristic IR absorptions in the vicinity of 3600 cm^{-1} and of high-field proton resonances (ca −2 to −6.5 ppm). The NMR data summarized in Table I unambiguously show that compounds **6** and **7** exist in solution as mixtures of the cis and trans isomers (structures I and II), while **8** is found exclusively as the trans isomer. For the methyl complex analogue, a mixture of cis and trans isomers had also been found in a ratio depending on the polarity of the solvent.[20] The cis and trans isomers of **6** and **7** readily interchange and are under thermodynamic equilibrium. In accord with this, the ^{1}H NMR spectrum of an approximately equimolar solution of **7** and **8**, shows, in addition to signals due to **7** and **8**, new sets of reasonances that can be attributed to the cis and trans isomers of the mixed derivative $(Me_3P)(PhMe_2CCH_2)Ni(\mu_2\text{-}OH)_2Ni(CH_2C_6H_5)(PMe_3)$. It is likely that traces of PMe$_3$ present in solution induce dissociation of the dimers to the 16-electron monomeric species NiR(OH)(PMe$_3$)$_2$. Formation of these intermediates and ulterior regeneration of the dimer would also imply exchange between coordinated and free PMe$_3$, and this has been confirmed by NMR studies of solutions that contain the hydroxides **6–8** plus added PMe$_3$.



I



II

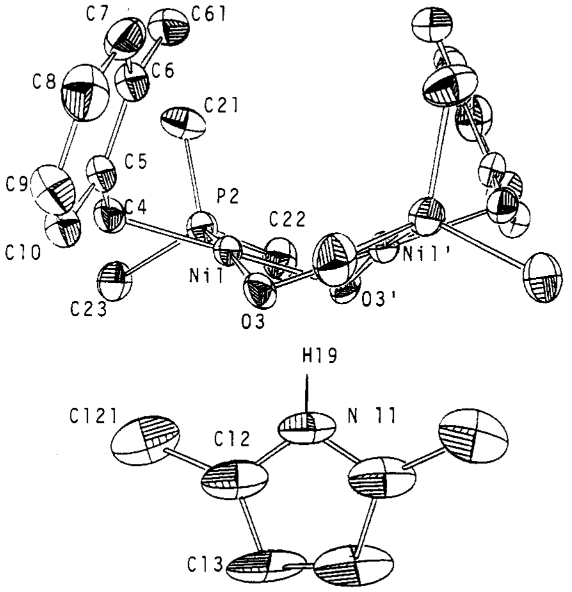


Figure 1. ORTEP diagram and atom-labeling scheme for $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2\cdot HNC_4H_2Me_2$.

Table II. Crystal Data for $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2\cdot HNC_4H_2Me_2$

empirical formula	$C_{28}H_{47}NO_2P_2Ni_2$
color	brown-red
cryst size, mm	0.40 × 0.40 × 0.67
space group	*C*2/*c*
cell dimens	
a, Å	15.598 (6)
b, Å	12.655 (7)
c, Å	17.705 (6)
β, deg	111.72 (4)
Z	4
V, Å^3	3243.7
D_{calcd}, g cm^{-3}	1.25
wavelength, Å	0.71069
temp, °C	19
mol wt	609.0
linear abs coeff, cm^{-1}	12.78
2θ range, deg	0–60
no. of unique data	6768
no. of data with [$I \geq 3\sigma(I)$]	2012
$R(F)$	0.057
$R_w(F)$	0.062

There is increasing interest in the structural characteristics of hydroxo derivatives of transition metals.[21] This, and the already mentioned formation of solid-state adducts between hydroxo compounds of nickel(II) and pyrrole derivatives have prompted us to undertake a single-crystal X-ray study of one of these adducts. The already reported[6] *o*-methylbenzyl complex $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2\cdot HNC_4H_2Me_2$, has been chosen for convenience. In addition to intrinsic interest, determination of the structure of this compound was of importance for comparative purposes. We have reported recently the results of an X-ray study carried out with the trimetallic compound $Ni_3(CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu\text{-}OH)_2$, and shown that the structure can be described[6] as consisting of a binuclear hydroxo-bridged fragment, $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2$ and a $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2$ group, the latter being stabilized by coordination of the nickel center to the two OH groups of the dimeric hydroxo unit. Compounds **6–8** and related derivatives provide the dimeric hydroxo fragment of the Ni$_3$ species. Not surprisingly, the donor properties of the bridging OH ligands are manifested again, although this time by their engagement in a fairly strong hydrogen-bonding interaction with the N–H bond of 2,5-dimethylpyrrole. An ORTEP drawing is shown in Figure 1. The compound consists of a dinuclear nickel-containing dihedral molecule (the two dihedral planes intersecting at the O(3)–O(3)′ direction; dihedral angle = 133.6°) and of a molecule of crystallization of 2,5-dimethylpyrrole, both of them situated on a 2-fold

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Table III. Bond Distances (Å) for $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2{\cdot}HNC_4H_2Me_2$

Ni(1)–P(2)	2.122 (2)	C(7)–C(8)	1.39 (1)
Ni(1)–O(3)	1.920 (4)	C(6)–C(7)	1.40 (1)
Ni(1)–O(3)′	1.917 (4)	C(8)–C(9)	1.35 (1)
Ni(1)–C(4)	1.946 (7)	C(9)–C(10)	1.38 (1)
P(2)–C(21)	1.813 (9)	N(11)–C(12)	1.33 (1)
P(2)–C(22)	1.812 (9)	N(11)–C(12)	1.33 (1)
P(2)–C(23)	1.821 (8)	N(11)–C(13)	2.14 (1)
C(4)–C(5)	1.49 (1)	N(11)–C(13)	2.14 (1)
C(5)–C(6)	1.39 (1)	C(12)–C(121)	1.48 (2)
C(5)–C(10)	1.38 (1)	C(12)–C(13)	1.37 (2)
C(6)–C(61)	1.49 (1)	C(13)–C(13)	1.31 (4)

Table IV. Bond Angles (deg) for $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2{\cdot}HNC_4H_2Me_2$

O(3)–Ni(1)–P(2)	97.0 (2)	C(8)–C(7)–C(6)	120.2 (10)
O(3)–Ni(1)–P(2)	172.3 (2)	C(9)–C(8)–C(7)	120.5 (10)
O(3)–Ni(1)–O(3)′	78.2 (3)	C(10)–C(9)–C(8)	119.5 (10)
C(4)–Ni(1)–P(2)	89.8 (2)	C(9)–C(10)–C(5)	122.4 (9)
C(4)–Ni(1)–O(3)′	173.1 (3)	C(12)–N(11)–C(12)	111.3 (6)
C(4)–Ni(1)–O(3)	95.0 (3)	C(13)–N(11)–C(12)	37.9 (9)
C(21)–P(2)–Ni(1)	114.0 (3)	C(13)–N(11)–C(12)	73.4 (10)
C(22)–P(2)–Ni(1)	118.4 (3)	C(13)–N(11)–C(12)	73.4 (10)
C(22)–P(2)–C(21)	102.9 (5)	C(13)–N(11)–C(12)	37.9 (9)
C(23)–P(2)–Ni(1)	113.8 (3)	C(13)–N(11)–C(13)	35.5 (9)
C(23)–P(2)–C(21)	103.4 (4)	C(121)–C(12)–N(11)	122.0 (12)
C(23)–P(2)–C(22)	102.5 (4)	C(121)–C(12)–N(11)	122.0 (12)
Ni(1)–O(3)–Ni(1)′	91.0 (2)	C(13)–C(12)–N(11)	105.5 (15)
C(5)–C(4)–Ni(1)	111.2 (5)	C(13)–C(12)–N(11)	105.5 (15)
C(6)–C(5)–C(4)	121.8 (8)	C(13)–C(12)–C(121)	132.4 (15)
C(10)–C(5)–C(4)	120.1 (8)	C(12)–C(13)–N(11)	36.6 (8)
C(10)–C(5)–C(6)	118.0 (9)	C(12)–C(13)–N(11)	36.6 (8)
C(61)–C(6)–C(5)	121.0 (9)	C(13)–C(13)–N(11)	72.2 (5)
C(7)–C(6)–C(5)	119.5 (9)	C(13)–C(13)–N(11)	72.2 (5)
C(7)–C(6)–C(61)	119.5 (9)	C(13)–C(13)–C(12)	108.8 (10)

crystallographic axis that contains the pyrrolic N–H group.

The geometry around each Ni atom is that of a distorted planar square, the O(3)–Ni(1)–O(3)′ bond angles being less than 90°, as expected from the fact that O(3) and O(3)′ are bridging atoms. Consequently, the O–Ni–C angles are greater than 90°, while the P–Ni–C ones remain unchanged from the ideal square-planar geometry (see Table IV). Each Ni atom is almost symmetrically bonded to the two hydroxyl groups, at Ni–O separations of 1.920 (4) and 1.917 (4) Å (for Ni(1)–O(3) and Ni(1)–O(3)′, respectively). Not unexpectedly, these values are appreciably smaller than all the Ni–O bond distances in $Ni_3(CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2$.[6]

An interesting feature of the compound is the existence of a symmetrical bifurcated[11] H bridge between the pyrrolic N atom and the O atoms of the nickel dimer. The N–O separations within the bridge are 3.12 (1) Å (1.00 (1) Å for the N–H bond, 2.230 (5) Å for the O···H interactions) and the angles at the hydrogen (N(11)–H(19)–O(3) and N(11)–H(19)–O(3)′) are both 147.1 (1)°.

(b) Binuclear Carbonate Complexes $(Me_3P)_2RNi(\mu_2\text{-}\eta^1,\eta^2\text{-}CO_3)NiR(PMe_3)$. The reaction of the pyrrolyl compounds **2a**,**b**, with high-purity commercial carbon dioxide under pressure (2–3 atm), affords the red crystalline complex **10**. Carefully dried CO_2 does not react with **2** under the same conditions, and in fact, deliberate addition of water to the reaction system is advisable, particularly for large-scale preparations. **10** is a binuclear species as revealed by a cryoscopic molecular weight determination. Its IR spectrum displays a strong absorption at ca. 1510 cm^{-1}, suggesting the existence of a carbonate ligand. Further evidence for this comes from the observation of a characteristic ^{13}C NMR resonance at ca. 170 ppm. On the basis of this and other data, **10** can be formulated as a binuclear, carbonate-bridged complex (eq 5). This has been confirmed by an X-ray study which shows

$$2NiR(NC_4H_2X_2)(PMe_3)_2 + CO_2 + H_2O \rightarrow Ni_2R_2(CO_3)(PMe_3)_3 + PMe_3 + 2HNC_4H_2X_2 \quad (5)$$

that the bridging carbonate ligand is dihapto bonded to one of the nickel atoms and monohapto bonded to the other. A drawing of the molecule of **10** is shown in Figure 2. The structure is however of poor quality (see Experimental Section), and therefore, the results of this study will not be discussed. There is precedent in the literature[22] for structures of the type found for **10**, and in addition, we have shown recently that the metalacycle $(Me_3P)_2\overline{Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4})$ reacts with CO_2 and H_2O, to provide[23] the neophyl analogue of **10**.

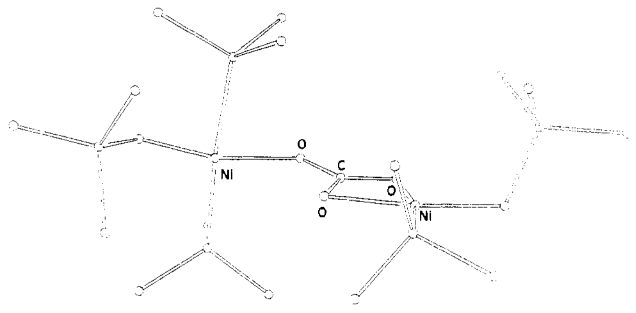
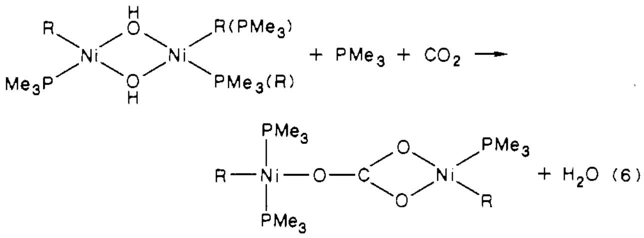


Figure 2. Drawing of the molecule of **10**.

Extension of the above synthetic procedure to other carbonate derivatives has proved unsuccessful. An alternative (and on the other hand general) route to these carbonates has been developed by means of hydroxo compounds of the type described in the last section (eq 6). By this route,[24] new compounds of composition



$Ni_2R_2(CO_3)(PMe_3)_3$ (R = CH_3 (**9**), CH_2SiMe_3 (**10**), $CH_2C_6H_5$ (**11**), C_6H_5 (**12**)) can be readily obtained and characterized. The transformation of eq 6 has also proved a more convenient procedure for the synthesis of the neophyl derivative, $Ni_2(CH_2CMe_2Ph)_2(CO_3)(PMe_3)_3$, which, as indicated above, had been produced previously by a different route.[23]

Compounds **9**–**12** are yellow to red crystalline solids, readily soluble in common organic solvents. Their IR spectrum is dominated by a strong absorption at ca. 1500 cm^{-1}, due to the carbonate ligand. They exhibit fluxional behavior in solution, but while **10** and the neophyl analogue give two separate ^{31}P resonances (ca. 2:1 ratio) in the room-temperature $^{31}P\{^1H\}$ NMR spectrum, the remaining compounds provide an average broad signal at approximately −10 ppm. The fluxional process responsible for this behavior has been described in detail elsewhere.[22,23b] Formation of these carbonates by action of CO_2 on the hydroxo complexes is an acid–base reaction. Whether this acid–base process is adequately represented by reaction 6 or requires catalytic or stoichiometric quantities of water (eq 7)

$$[NiR(PMe_3)(\mu\text{-}OH)]_2 + PMe_3 + H_2CO_3 \rightarrow Ni_2R_2(CO_3)(PMe_3)_3 + 2H_2O \quad (7)$$

cannot be ascertained. It should be recalled that complete removal of small amounts of water from CO_2 is difficult to achieve. Finally, it should be mentioned that in order to avoid the unnecessary loss of PMe_3 implied in the isolation of the hydroxo compounds

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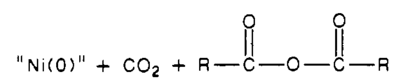
(24) A recent report by Caulton has described the formation of a rhodium carbonate complex from the reaction of CO_2 with a dimeric rhodium hydroxo species. See: Lundquist, E. G.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1987**, *26*, 205.

$[Ni(R)(PMe_3)(\mu\text{-}OH)]_2$, the carbonates **9**–**12** can be obtained by direct action of CO_2 upon the supernatant which results after the separation of the excess of powdered NaOH in reaction 4.

The carbonate–neophyl species $Ni_2(CH_2CMe_2Ph)_2(CO_3)(PMe_3)_3$ has been shown to undergo an unusual transformation in the presence of carbon monoxide, which yields, in addition to $Ni(CO)_n(PMe_3)_{4-n}$ ($n = 2, 3$), carbon dioxide and the anhydride $(RCO)_2O$. The generality of this carbonate–carbonyl conproportionation reaction[23] has been attested by studying the interaction of the carbonates **9**–**12** with CO. As shown in eq 8, all



$$Ni_2R_2(CO_3)(PMe_3)_3 \xrightarrow{CO} \text{"Ni(0)"} + CO_2 + R\text{—}\overset{O}{\overset{\|}{C}}\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{—}R \qquad (8)$$

the carbonates react in the expected manner, although for simplicity, only the reactions of **9** and **12** have been studied in detail (see Experimental Section).

Experimental Section

Microanalyses were by Pascher, Microanalytical Laboratory, Bonn. The spectroscopic instruments used were Perkin-Elmer Models 577 and 684 for IR spectra and Varian Model XL-200 for NMR. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C NMR spectra were referenced by using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$.

All preparations and other operations were carried out under a protective blanket of oxygen-free nitrogen, following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had a boiling point range of 40–60 °C. $NaNC_4H_4$ and $NaNC_4H_2\text{-}2,5\text{-}Me_2$ were prepared by reacting NaH with pyrrole and 2,5-dimethylpyrrole, respectively. The anhydrous CO_2, required for some of the preparations, was obtained by reaction of $BaCO_3$ with H_2SO_4 and purified by several trap-to-trap distillations. The alkyl derivatives *trans*-$Ni(R)Cl(PMe_3)_2$ (R = CH_3,[25] CH_2SiMe_3,[12b] CH_2CMe_3,[26] CH_2CMe_2Ph,[12b] $CH_2C_6H_5$,[27] 2,4,6-$C_6H_2Me_3$[27]) were prepared as described in the literature. The ligand PMe_3 was obtained by the method of Wolfsberger and Schmidbaur.[28] All new compounds gave satisfactory elemental analyses.

Pyrrolyl Derivatives of Composition $Ni(R)(2,5\text{-}NC_4H_2X_2)(PMe_3)_2$ (1a,b–5a,b). All the pyrrolyl complexes reported in this work have been prepared by reacting the corresponding alkyl derivative $Ni(R)Cl(PMe_3)_2$ with the appropriate pyrrolyl sodium salt $NaNC_4H_2X_2$ (X = H, Me), following the procedure described below for complex **3a**, $Ni(CH_2CMe_3)(NC_4H_4)(PMe_3)_2$.

To a stirred solution of the alkyl $Ni(CH_2CMe_3)Cl(PMe_3)_2$ (0.73 g, ca. 2.3 mmol), in Et_2O (40 mL), cooled at −30 °C, an excess of $NaNC_4H_4$ (3 mL of a 1 M solution in THF) was added. The resulting mixture was stirred for 15 min, slowly warmed to room temperature, and then further stirred for 4–5 h, during which time the color of the solution changed from brown-red to yellow-orange. The solvent was removed under vacuum and the residue extracted with Et_2O (20 mL). After centrifugation and partial concentration of the solution, cooling at −30 °C for several hours provided orange crystals of the desired compound (yield 60%).

The complexes $Ni(CH_2SiMe_3)(NC_4H_4)(PMe_3)_2$ (**2a**) and the neophyl analogue (**4a**) were also isolated as yellow-orange crystals in 60% yield from Et_2O solutions. The more soluble $Ni(Me)(NC_4H_4)(PMe_3)_2$ (**1a**) and $Ni(2,4,6\text{-}C_6H_2Me_3)(NC_4H_4)(PMe_3)_2$ (**5a**) were crystallized from petroleum ether, in comparable or higher yields. The 2,5-dimethylpyrrolyl derivatives **1b**–**5b** were prepared similarly, but the dry residues of the reactions were extracted with a mixture petroleum ether–diethyl ether and worked up by following the same procedure, to afford red-orange crystalline materials in 60–70% yields. The methyl derivative $Ni(Me)(NC_4H_2Me_2)(PMe_3)_2$ (**1b**) was sometimes obtained mixed with a small amount of the pyrrole adduct $Ni(Me)(NC_4H_2Me_2)(PMe_3)_2\cdot HNC_4H_2Me_2$.

Reaction of the Pyrrolyl Derivatives with CO. The study of the reactivity of these complexes with CO has been carried out with both the pyrrolyl and the 2,5-dimethylpyrrolyl derivatives of CH_2SiMe_3 (**2a,b**) and 2,4,6-$C_6H_2Me_3$ (**5a,b**). The results are described below.

(a) Reaction of Compounds 2 with CO. CO was bubbled through a solution of compounds **2** (ca. 2 mmol) in Et_2O (30 mL) at room temperature and atmospheric pressure, for 10 min, during which time the color of the solution changed from red-orange to pale yellow. The solvent was evaporated under reduced pressure and the resulting pale yellow oily residue demonstrated by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopies to contain a mixture of the amide $Me_3SiCH_2C(O)NC_4H_4$ and $Ni(CO)_2(PMe_3)_2$ (reaction of **2a**). $Me_3SiCH_2C(O)NC_4H_4$: ^1H NMR (200 MHz, C_6D_6) δ −0.10 (s, 9 H, $SiMe_3$), 2.10 (s, 2 H, CH_2Si), 6.05 and 7.10 (s, 2 H and 2 H, NC_4H_4); $^{13}C\{^1H\}$ NMR (C_6D_6) δ −1.6 ($SiMe_3$), 27.1 ($SiCH_2$), 112.3 and 119.1 (NC_4H_4), 168.8 (CO); IR (Nujol mull) ν_{CO} at 1700 cm^{-1}. For the 2,5-dimethylpyrrolyl complex, **2b**, the spectroscopic studies also indicate the formation of the corresponding amide, $Me_3SiCH_2C(O)NC_4H_2Me_2$, and the carbonyl $Ni(CO)_2(PMe_3)_2$. $Me_3SiCH_2C(O)NC_4H_2Me_2$: ^1H NMR (200 MHz, C_6D_6) δ −0.08 (s, 9 H, $SiMe_3$), 2.04 and 2.21 (s, 3 H and 3 H, $NC_4H_2Me_2$), 2.19 (s, CH_2Si), 5.71 and 5.81 (s, 1 H and 1 H, $NC_4H_2Me_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ −1.7 ($SiMe_3$), 12.9 and 16.0 ($NC_4H_2Me_2$), 32.1 (CH_2Si), 105.9 and 110.7 (CH pyrrole), 125.0 and 129.0 (quaternary C, pyrrole), 173.3 (CO); IR (Nujol mull) ν_{CO} at 1710 cm^{-1}.

(b) Reaction of $Ni(2,4,6\text{-}C_6H_2Me_3)(NC_4H_2X_2)(PMe_3)_2$ (5) with CO. Complex **5a** does not react with CO under ambient conditions. Nevertheless, when a solution of **5a** was pressurized (2–3 atm CO) and stirred for 4–5 h at room temperature, it was observed to become colorless. Subsequent spectroscopic studies (IR, ^1H, ^{13}C and ^{31}P NMR) indicated the formation of the amide 2,4,6-$C_6H_2Me_3C(O)NC_4H_4$ and the complexes $Ni(CO)_2(PMe_3)_2$ and $Ni(CO)_3(PMe_3)$. 2,4,6-$C_6H_2Me_3C(O)NC_4H_4$: ^1H NMR (200 MHz, C_6D_6) δ 1.95 (s, 6 H, 2 Me), 2.10 (s, 3 H, Me), 6.00, 6.20, 6.32, and 7.70 (br s, 1, 1, 1, and 1 H, NC_4H_4), 6.62 (s, 2 H, $C_6H_2Me_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 18.6 (2 Me), 20.8 (Me), 113.3, 113.6, 118.0, and 120.8 (CH pyrrole), 128.2 (CH, $C_6H_2Me_3$ group), 132.2, 134.4, and 139.2 (quaternary aromatic carbons), 168.0 (CO). IR (Nujol mull): ν_{CO} at 1710 cm^{-1}. The 2,5-dimethylpyrrolyl derivative **5b** did not react with CO when stirred for 4 days, under 2–3 atm of CO.

Dimeric μ-Hydroxide Derivatives of Composition $[NiR(PMe_3)(\mu\text{-}OH)]_2$. These μ-hydroxide derivatives were obtained from the parent compounds $Ni(R)Cl(PMe_3)_2$, following the method described below for the benzyl derivative $[Ni(CH_2C_6H_5)(PMe_3)(\mu\text{-}OH)]_2$ (**8**).

A mixture of $Ni(CH_2C_6H_5)Cl(PMe_3)_2$ (0.5 g, ca. 1.5 mmol) and an excess of powdered NaOH (0.5 g) was stirred in THF (30 mL) at room temperature for 3–4 h. The color of the solution changed from red-brown to orange. The solvent was stripped-off and the residue extracted with a mixture of petroleum ether–diethyl ether (1:2) and centrifuged. After partial evaporation of the solvent, cooling of the resulting solution furnished dark-red crystals of the title compound in nearly quantitative yield.

Similar procedures allowed the isolation of the related derivatives $[Ni(CH_2CMe_2Ph)(PMe_3)(\mu\text{-}OH)]_2$ (**7**) (as brown yellow needles, from petroleum ether), $[Ni(CH_2SiMe_3)(PMe_3)(\mu\text{-}OH)]_2$ (**6**) (red-brown plates, from petroleum ether) and $[Ni(C_6H_5)(PMe_3)(\mu\text{-}OH)]_2$ (yellow microcrystals, from mixtures of petroleum ether–dichloromethane (2:1)). The latter complex was not analyzed, and it is reported only for comparative purposes. Compound **6** can also be prepared, albeit in lower yields, by the following procedure. To a stirred solution of the dialkyl $Ni(CH_2SiMe_3)_2(PMe_3)_2$ (0.6 g, 1.5 mmol) in acetone (30 mL) was added a drop of water. The stirring was continued for 10–12 h and the solvent removed under vacuum. The residue was dissolved in petroleum ether, and after centrifugation, concentration and cooling of the solution at −30 °C, red-brown plates of the dimeric μ-hydroxo complex were obtained in 40% yield.

Reaction of the Dimeric μ-Hydroxo Derivatives with CO_2: Synthesis of the Carbonate-Bridged Complexes $(Me_3P)(R)Ni(\mu_2\text{-}\eta^2,\eta^1\text{-}CO_3)Ni(R)(PMe_3)_2$. The suspension containing the appropriate dimeric μ-hydroxide complex, obtained by stirring the alkyl derivative with NaOH, was filtered into a thick-wall vessel, which was pressurized with 3 atm of CO_2 and stirred at room temperature for 3 h. The solvent was evaporated under vacuo and the resulting residue extracted with the adequate solvent (see below) and centrifuged. Partial evaporation and cooling at −30 °C provided crystals of the desired compounds in almost quantitative yields: R = Me (**9**), yellow-brown plates from petroleum ether–diethyl ether (1:2); R = CH_2SiMe_3 (**10**), dark-red needles from petroleum ether; R = $CH_2C_6H_5$ (**11**), orange needles, from diethyl ether; R = C_6H_5 (**12**), yellow microcrystals, from petroleum ether–diethyl ether (1:2). The CH_2SiMe_3 derivative **10** was also obtained by the reaction of petroleum ether solutions of the pyrrolyl derivatives $Ni(CH_2SiMe_3)(NC_4H_2X_2)(PMe_3)_2$ (ca. 1 mmol in 40 mL of solvent) with wet CO_2 (2.5 atm, 24 h) in 60% yield.

Reaction of the Bridging Carbonate Derivatives 9 and 12 with CO. A solution of the carbonate (ca. 1 mmol) in 0.5 mL of C_6D_6 was stirred

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under 2 atm of CO for 15-30 min. The color of the solution became pale yellow. ^{1}H, ^{31}P, and ^{13}C NMR studies of the resulting solution, together with the IR spectrum of the residue obtained by removal of the solvent, allowed the identification of the organic anhydride $(RCO)_2O$ and of the carbonyls $Ni(CO)_2(PMe_3)_2$ and $Ni(CO)_3(PMe_3)$ as the only detectable products.

X-ray Structure Determination. The air-sensitive crystal of $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2{\cdot}HNC_4H_2Me_2$ was put in a glass capillary under nitrogen atmosphere and mounted on the goniometer head of an Enraf-Nonius CAD4 diffractometer. Data were collected by using ω-2θ scans and reduced, and a set of 2012 unique reflections was used in subsequent calculations. The analysis of the Patterson map permitted the location of the Ni atoms, the rest of the non-H atoms being located by means of successive cycles of Fourier synthesis. The H atoms were geometrically placed, except the one corresponding to the NH group (extracted from a Fourier difference map). The H atoms corresponding to the OH groups could not be found, and its consideration was omitted. An empirical absorption correction[29] was applied at the end of the isotropic refinement of the non-H atoms but some degree of disorder, nonresolvable from thermal motion, was encountered in the pyrrolyl carbon atoms. The anisotropic refinement converged at $R = 0.057$, using unit weights. A summary of crystal data is given in Table II. All computations were made with the Oxford CRYSTALS package.[30] The atomic scattering factors were taken from ref 31.

Figure 2 shows the geometry of the molecule of **10**. Although the structure has been solved in the triclinic space group $P1$, all attempts to refine it below $R \simeq 20$ (convergence of isotropic refinement) have proved unsuccessful, and thus no crystallographic data are included.

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Supplementary Material Available: Analytical data for complexes **1**-**11** and ^{1}H, ^{31}P, and ^{13}C NMR data for the pyrrolyl complexes **1**-**5** (Tables A, B, and C), fractional atomic coordinates and thermal parameters for $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2{\cdot}HNC_4H_2Me_2$ (Tables D and E) (4 pages); observed and calculated structure factors (Table F) (19 pages). Ordering information is given on any current masthead page.

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Preparation of $(\eta\text{-}C_5H_5)W(CO)_2(PPh_3)SR$ and Insertion of CS_2 To Give the Thioxanthates $(\eta\text{-}C_5H_5)W(CO)_2S_2CSR$ ($R = CHMe_2, CH_2Ph, 4\text{-}C_6H_4Me$). Crystal Structure of $(\eta\text{-}C_5H_5)W(CO)_2S_2CSCH_2Ph$

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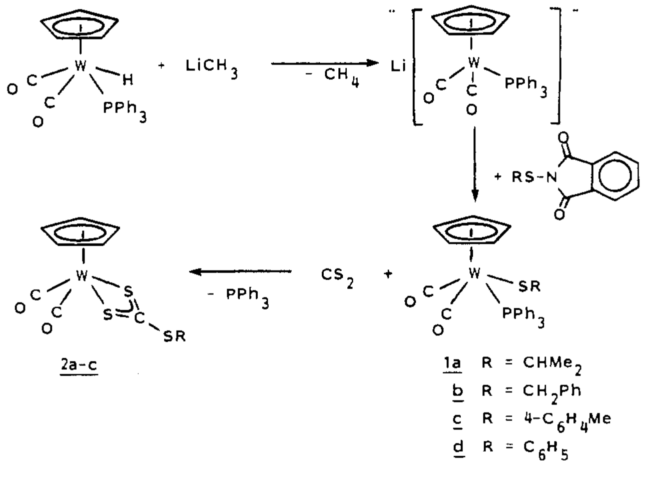
Treatment of $(\eta\text{-}C_5H_5)W(CO)_2(PPh_3)H$ with methyllithium and subsequently with RS(phth) gave $(\eta\text{-}C_5H_5)W(CO)_2(PPh_3)SR$ as a mixture of cis and trans isomers, where phth = phthalimido and $R = CHMe_2$, CH_2Ph, and $4\text{-}C_6H_4Me$. These isomers react with CS_2 to give the thioxanthate complexes $(\eta\text{-}C_5H_5)W(CO)_2S_2CSR$ wherein the CS_2 has inserted into the W-SR bond. The structure of $(\eta\text{-}C_5H_5)W(CO)_2S_2CSCH_2Ph$ was determined: $C2/c$, $a = 27.106$ (20) Å, $b = 10.050$ (5) Å, $c = 13.108$ (13) Å, $\beta = 66.18$ (7)°, $V = 3266.4$ Å^3, and $Z = 8$. The cis isomer reacted more rapidly than the trans; the reaction was retarded by the presence of free PPh_3 or CO. The implications with respect to the mechanism of CS_2 insertion are discussed.

Introduction

Preparative routes to thiolato complexes of the type $CpW(CO)_3SR$, where Cp = η^5-cyclopentadienide and R = alkyl and aryl, are well developed.[2] As part of our studies on polysulfano tungsten[3] complexes, the triphenylphosphine-substituted complexes $CpW(CO)_2(PPh_3)SR$ were required. Those with $R = C_6H_5$ and $4\text{-}C_6H_4Me$ have recently been prepared via a complicated photochemical route and were not isolated in the pure state.[4] This paper reports the preparation of the desired complexes by a mild and general route. The presence of the triphenylphosphine ligand renders the complexes susceptible to further reactions. Specifically, it was found that CS_2 easily inserts into the tungsten-thiolate bond to give the thioxanthate complexes $CpW(CO)_2S_2CSR$.

Scheme I



Results

Treatment of $CpW(CO)_2(PPh_3)H$[5] in THF at 0 °C, first with MeLi and subsequently with RS(phth),[6] where phth = phthalimido, gave the complexes $CpW(CO)_2PPh_3SR$ (**1a**-**d**) (Scheme

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(1) (a) McGill University. (b) Concordia University.

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