by dissolving the mixture in a minimum amount of acetone, adding a few drops of ether, and allowing the clear solution to stand overnight at room temperature. The crystals were washed with acetone/ether (8:3) to remove the α-isomer. The pure β-isomer, 95 mg, was obtained [mp 288–290 °C; IR (KBr) ν_{CO} 1752 cm^{-1}]. The pure α-isomer, 101 mg, was obtained [mp 155–157 °C: IR (KBr) ν_{CO} 1750 cm^{-1}] by repeating the above process several times.

When the above synthesis was carried out in 70 mL of 1,2-dichloroethane, the α and β ratio was the same, i.e., 7:3.

X-ray Structure Determination of 2b. An automated Nicolet R3m diffractometer with incident beam graphite monochromator and Cu Kα X-rays (λ = 1.54178 Å) was used to collect the intensities of 1989 reflections [2θ(max) = 120.0°]. Of these, 1847 were unique (nonredundant) data and 1837 were considered observed [$F_o > 3\sigma(F_o]$. Empirical absorption corrections were estimated from psi-scan observations on 20 selected reflections; minimum and maximum transmission coefficients were 0.51 and 0.98, respectively. The structure was solved by direct methods and refined by using full-matrix least-squares methods contained in the program package SHELXTL.[29] The quantity $\sum w(F_o - F_c)^2$ was minimized, where $w = 1/[\sigma^2(F_o + gF_o^2]$ ($g = (0.015)^2$). Final refinement with 379 variables (H atoms isotropic, all others anisotropic) yields R_1 = 0.0251, R_2 = 0.0325, and $S = [(\sum w\Delta^2)/(N_o - N_p)]^{1/2}$. Maximal ripples in the final Fourier difference map were 0.44 and –0.73 e Å^{-3}.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the Natural Sciences and Engineering Research Council of Canada (M.J.M) is gratefully acknowledged.

Supplementary Material Available: Tables of anisotropic temperature factors and H-atom coordinates (2 pages); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Formation of Alkenyl Ketone Complexes and of Dimeric α,β-Butenolides by Sequential Insertion of Phenylacetylene and Carbon Monoxide into Nickel–Acyl Bonds. X-ray Structures of Ni[C(Ph)=C(H)(COCH$_2$SiMe$_3$)]Cl(PMe$_3$)$_2$ and Ni[C(Ph)(PMe$_3$)C(H)(COCH$_2$CMe$_2$Ph)]Cl(PMe$_3$)

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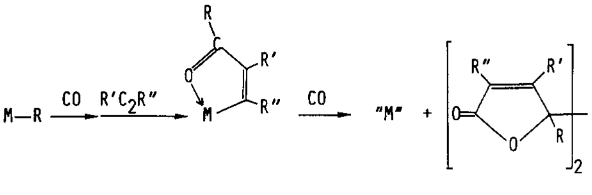
The insertion of PhC≡CH into the nickel–carbon bond of the acyls *trans*-Ni(COR)Cl(PMe$_3$)$_2$ is highly regio- and stereoselective and provides goods yields of *trans*-(*Z*)-Ni[C(Ph)=C(H)(COR)]Cl(PMe$_3$)$_2$ (R = CH$_3$, **1a**; R = CH$_2$SiMe$_3$, **1b**; R = CH$_2$CMe$_3$, **1c**; R = CH$_2$C$_6$H$_4$-*o*-Me, **1d**; R = CH$_2$CMe$_2$Ph, **1e**). The nickel center in these complexes is in a five-coordinate distorted square-pyramidal environment, as demonstrated by an X-ray study carried out with the CH$_2$SiMe$_3$ derivative **1b**. The neophyl complex **2e** undergoes a reversible 1,2 trimethylphosphine shift and rearranges to the nickelacyclopropane complex Ni[C(Ph)(PMe$_3$)C(H)(COCH$_2$CMe$_2$Ph)]Cl(PMe$_3$) (**2**) whose structure has also been determined by X-ray crystallography. Complex **1b** is monoclinic of space group $P2_1/n$, while **2** is orthorhombic of space group *Pbca*. **1b** has unit cell parameters a = 12.532 (8) Å, b = 14.099 (1) Å, c = 14.36 (1) Å, β = 98.51 (6)°, and D(calcd) = 1.23 g cm^{-3} for Z = 4. Corresponding values for **2** are a = 20.638 (5) Å, b = 20.09 (1) Å, c = 12.913 (5) Å, and D(calcd) = 1.26 g cm^{-3} for Z = 8. The keto vinyl complexes **1** react smoothly with CO (20 °C, 1 atm) with formation of dimers of γ-but-2-enolactone, **3**, in good yields. Formation of these dimeric α,β-butenolides can be achieved in a one-pot synthesis, starting from the alkyls NiCl(R)(PMe$_3$)$_2$, by successive insertion of CO, PhC≡CH, and CO.

At variance with the large number of investigations concerning the addition of M–R bonds to carbon monoxide,[2] studies related to the insertion of alkynes into transition metal–alkyl bonds have been explored less.[3]

Scheme I



Sequential insertion of carbon monoxide and an alkyne is an attractive reaction of potential importance for the synthesis of organic molecules.[4] Very often, the resulting

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(1) (a) Universidad de Sevilla-CSIC. (b) Universidad Complutense de Madrid-CSIC.

(2) See, for example: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA 1987.

(3) (a) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002. (b) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Healthcoch, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022. (c) Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.

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Table I. Analytical and $^{31}P\{^1H\}$ and ^1H NMR Data for 1a–e and 2

	analytical data[b]			^1H[a] δ (*J*, Hz)			
	C	H	$^{31}P\{^1H\}$ δ	PMe_3[c]	=CH	CH_2	CH_3
1a[d]	49.0 (49.2)	7.0 (6.9)	−16.3 (s)	0.98 (t, 4.0)	6.73 (t, 4.5)		2.17 (s)
1b	48.8 (49.2)	7.5 (7.5)	−16.3 (s)	0.96 (t, 4.0)	6.76 (t, 5.2)	2.25 (s)	0.12 (s)
1c	53.1 (53.6)	7.7 (7.8)	−16.4 (s)	0.96 (t, 4.1)	6.74 (t, 4.5)	2.38 (s)	1.14 (s)
1d	57.2 (57.3)	6.9 (6.8)	−16.5 (s)	0.86 (t, 4.0)	*e*	3.78 (s)	2.35 (s)
1e	59.1 (58.9)	7.4 (7.3)	−16.5 (s)	0.83 (t, 4.0)	6.49 (t, 4.4)	2.77 (s)	1.51 (s)
2	58.0 (58.9)	7.2 (7.3)	14.7 (d) −14.6 (d) *J*(PP) = 15 Hz	1.02 (d, 7.0) 1.46 (d, 14.0)	2.99 (d, 25.0)	2.63 (d) 2.09 (d) *J*(HH) = 12.0 Hz	1.64 (s) 1.36 (s)

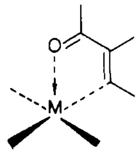
[a] Multiplets for C_6H_5 protons between δ 7.1 and δ 8.4. [b] Calculated values in parentheses. [c] Apparent or real J_{HP}. [d] Cl: 7.7 (7.7). [e] Obscured by phenyl resonances.

Table II. $^{13}C\{^1H\}$ NMR Data for 1a–e

	$^{13}C\{^1H\}$[a] δ						
	PMe_3[b]	Ni–C	=CH	C_6H_5	CO	CH_2	CH_3
1a	13.0 (t, 13.6)	206.2 (t, 32.3)	126.4 (t, 4.0)	128.0 (s, 2CH), 128.5 (s, 2CH) 129.1 (s, CH), 144.0 (s, C)	196.5 (s)		30.2 (s)
1b	13.0 (t, 13.5)	203.7 (t, 33.1)	127.4 (t, 4.0)	127.9 (s, 2CH), 128.4 (s, 2CH) 128.7 (s, CH), 144.4 (s, C)	197.5 (s)	38.1 (s)	−1.0 (s)
1c[c]	13.1 (t, 13.7)	206.9 (t, 32.4)	*d*	128.0 (s, 2CH), 128.6 (s, 2CH) 129.0 (s, CH), 144.4 (s, C)	199.3 (s)	55.9 (s)	30.1 (s)
1d[e]	12.8 (t, 13.8)	*d*	*d*	127.9 (s, 2CH), 128.4 (s, 2CH) 129.0 (s, CH), 144.2 (s, C)	196.4 (s)	19.9 (s)	48.3 (s)
1e[f]	12.9 (t, 13.5)	*d*	*g*	128.1 (s, 2CH), 128.5 (s, 2CH) 128.8 (s, CH), 144.4 (s, C)	198.0 (s)	56.2 (s)	29.7 (s)

[a] *J* values in parentheses in Hz. [b] Apparent J_{PC}. [c] δ 31.6 (s, CMe_3). [d] Not observed. [e] δ 126.1 (s), 126.7 (s), 130.3 (s) 130.4 (s) (R, aromatic *C*H), 135.3 (s), 136.7 (s) (R, aromatic *C*). [f] δ 37.9 (s, CMe_2), 125.5 (s), 125.9 (s), 127.9 (s) (R, aromatic *C*H), 149.0 (s) (R, aromatic *C*). [g] Obscured by solvent resonance.

keto vinyl complexes are stabilized by a secondary interaction that involves the oxygen atom of the original acyl group, yielding five-membered metallacycles[5,6] of type I.

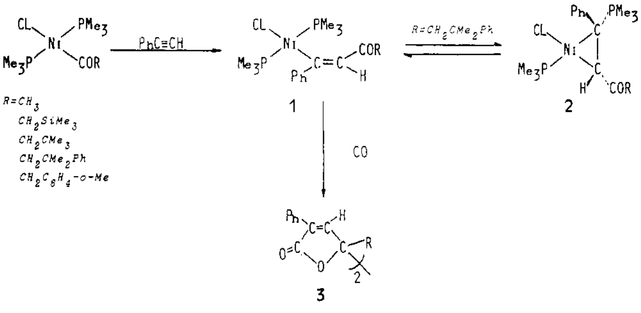


I

The existence in these compounds of a transition metal–carbon bond suggests further insertion chemistry can be carried out, and this together with the ability of the strong π-acid carbon monoxide ligand to induce elimination of the organic fragment, following insertion, provides the basis for the dessign of a rational synthetic route to α,β-unsaturated γ-lactones, i.e. α,β-butenolides (Scheme I). These five-membered unsaturated lactones are important synthetic targets.[4,7] The α,β-butenolide ring is, for instance, present in a large number of biologically important natural products, and, on the other hand, certain butenolides exhibit antitumor, antifungal, and antibacterial activities.

In this paper we wish to report the sequential insertion of an unactivated alkyne, PhC≡CH, and carbon monoxide into the nickel–carbon bond of the acyls *trans*-Ni(COR)Cl(PMe_3)$_2$, with initial regio- and stereoselective formation of the keto vinyl complexes *trans*-(*Z*)-Ni[C(Ph)=CHCOR]Cl(PMe_3)$_2$ (**1a–e**) and then of the dimeric α,β-butenolides [CH=C(Ph)C(O)OC(R)–]$_2$ (**3**) as shown in Scheme II. The neophyl derivative **1e** reversibly rearranges to a nickelacyclopropane compound, Ni[C(Ph)(PMe_3)C(H)($COCH_2CMe_2Ph$)]Cl(PMe_3) (**2**), which contains a novel ketoylidic ligand. The X-ray structures of **1b** and **2** have been determined and are also reported. Part of this work has appeared in preliminary form.[8] Analytical and spectroscopic data for new compounds are in Tables I and II and in the supplementary material (Tables A and B, data for compounds **3**).

Scheme II



Results and Discussion

Formation of the Keto Alkenyl Complexes *trans*-(*Z*)-Ni[C(Ph)=C(H)(COR)]Cl(PMe_3)$_2$ (1a–d). The Crystal and Molecular Structure of 1b (R = CH_2SiMe_3).

Treatment of the acyl complexes *trans*-Ni(COR)Cl(PMe_3)$_2$ (R = CH_3, CH_2SiMe_3, CH_2CMe_3,

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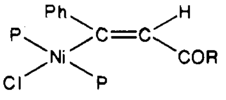
(8) Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1984**, *3*, 1438.

$CH_2C_6H_4$-o-Me), with phenylacetylene, results in the formation of the red-brown crystalline complexes **1a–d**. Compounds 1 are moderately air-stable in the solid state but very sensitive in solution. They are very soluble in common organic solvents in which they behave as nonelectrolyte species. Elemental analysis reveal they result from the formation of 1:1 addition products between the alkyne and the corresponding acyl. The IR spectra of the new compounds display ν(C–O) at ca. 1600 cm^{-1}, that is, 40–50 cm^{-1} lower than in the parent acyls, and this suggests that a change in the coordination mode of the acyl ligand has taken place.

Spectroscopic studies demonstrate that compounds 1 have trans phosphine ligands and are the products of the insertion of the alkenyl into the Ni–C bond of the acyls *trans*-$Ni(COR)Cl(PMe_3)_2$. Although this insertion reaction may in principle yield alkenyl complexes with four possible structures (II–V), ^1H NMR studies of equimolar mixtures of *trans*-$Ni(COCH_2SiMe_3)ClPMe_3)_2$ and PhC≡CH demonstrate the reactions are highly regio- and stereoselectives and yield a single isomer. Structures II and III correspond to the products of the cis and trans addition, respectively, of the Ni—COR group across the C≡C bond, with the phenyl group of the original alkyne next to the nickel atom, while IV and V are the analogous cis and trans addition products having the phenyl group at the vinylic C_β position. The ^1H and the ^{13}C NMR spectra of compounds 1 are strongly indicative of cis addition of type II, and therefore formation of these alkenyl complexes occurs as depicted in eq 1. The proposed stereochemistry is supported by the large carbon to phosphorus and proton to phosphorus coupling constants between the α-vinylic carbon or the hydrogen atom directly attached to C_β on one side ($^2J_{PC}$ = 33.1 Hz; $^4J_{PH}$ = 5.2 Hz, data for **1b**) and the two equivalent phosphorus nuclei on the other. Decisive support for this proposal comes from a single-crystal structure determination, to be discussed below, carried out with complex **1b**, which demonstrates this compound has trans *Z* geometry. Similar regioselectivity is observed in the analogous insertion of alkynes into the Ni-alkyl bond of the complex $Ni(acac)CH_3(PPh_3)$[3a] and also in the insertion of unsymetrical alkynes into the M–COR bonds of molybdenum and tungsten acyls.[5] However, formation of the other regioisomer has been found in the reaction of $(C_5Me_5)Cr(CO)_3(CH_3)$ with PhC≡CH, which affords $(C_5Me_5)(CO)_2Cr[C(H){=}C(Ph)COMe]$.[5e] As reported for the nickel–acac complex,[3a] we believe that migration of the acyl group to the less hindered alkyne carbon is steric in origin. In fact, the reaction of PhC≡CPh with the acyls *trans*-$Ni(COR)Cl(PMe_3)_2$ (R = CH_2CMe_2Ph, $CH_2C_6H_4$-o-Me), under similar conditions, provides only the unreacted acyls.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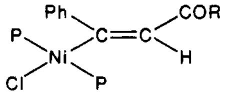
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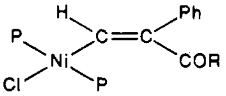
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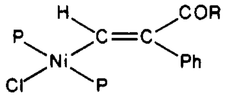
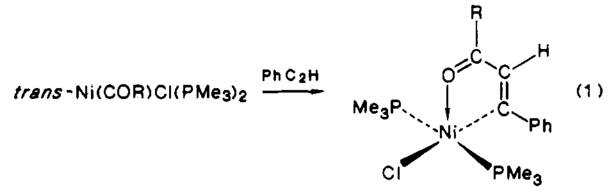
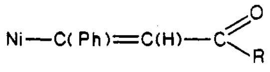
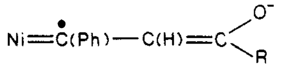

V


(1)

1a, R = CH_3
b, R = CH_2SiMe_3
c, R = CH_2CMe_3
d, R = $CH_2C_6H_4$-o-Me

Formation of related keto vinyl complexes has been observed previously. For instance, the photoinduced reaction[5] of (η^5-Ar)$M(CO)_3R$ (η^5-Ar = η^5-C_5H_5 or related ligands; M = Cr, Mo, W; R = Me, Et, Pr^n, Bu^n) with alkynes, $R^1C{\equiv}CR^2$, provides alkenyl ketone complexes of the type (η^5-Ar)$(CO)_2M[C(R^1){=}C(R^2)(COR)]$, for which spectroscopic and X-ray structural data[5d] indicate considerable double-bond character for the M–C_α bond. A similar situation, although less pronounced, is found in the nickel compounds 1, for which the chemical shift of the nickel-bound carbon atom, Ni—*C*(Ph)=, appears at the low field value of ca. 203 ppm, i.e. at appreciably lower field than expected for a normal M–C_α vinylic atom.[9] This probably reflects some contribution of the carbenoid resonance form VII to the ground state of these molecules,


VI


VII

and it is in good agreement with the electrophilic character displayed by the Ni–C_α carbon atom in the neophyl complex $Ni[C(Ph){=}C(H)(C(O)CH_2CMe_2Ph)]Cl(PMe_3)_2$ (**1e**) which, as discussed below, undergoes a reversible 1,2 shift of one of the PMe_3 ligands, with formation of a nickelacyclopropane complex that contains formally a novel, 1-(trimethylphosphonio)-1-phenyl-2-(neophylacyl)ethylene ligand, $[(P^+Me_3)(Ph){=}C(H)(COCH_2CMe_2Ph)]$, η^2-coordinated to the metal atom through the C=C bond (see below).

The above proposal concerning the alkenyl stereochemistry in compounds 1 is based on NMR studies. In order to unambiguously characterize the vinyl geometry, an X-ray study on a representative compound, $Ni[C(Ph){=}C(H)(COCH_2SiMe_3)]Cl(PMe_3)_2$ (**1b**), has been undertaken. Single crystals of this complex were obtained from diethyl ether and were shown to correspond to the trans *Z* isomer, i.e. the product of the 1,2 cis addition of the Ni—COR group across the C≡C bond of the alkyne. The crystals are monoclinic, space group $P2_1/n$, and the structure has been solved by Patterson and Fourier techniques and refined by least-squares methods to give a final *R* value (unit weights) of 0.056. Details of the structure determination are given in the Experimental Section, an ORTEP drawing of **1b** is displayed in Figure 1, and a summary of crystal structure data and bond distances and angles are collected in Tables III–V. The nickel atom is in a five-coordinate distorted square-pyramidal environment, with the keto vinylic oxygen O(1) in the apical position, at a distance of 2.535 (7) Å. Similar contacts have been observed in related complexes[10] and correspond, in general, to relatively weak bonding interactions.[5d] As expected, this distance is appreciably longer than that corresponding to a normal Ni–O bond (ca. 1.90–2.00 Å[11]), and

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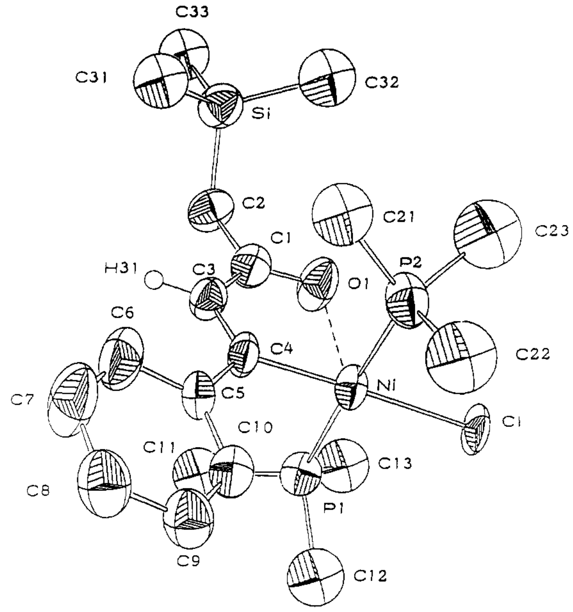

Figure 1. ORTEP diagram for **1b** and atom-labeling scheme.

Table III. Summary of Crystal Data

	1b	2
empirical formula	$C_{19}ClH_{35}NiOP_2Si$	$C_{26}ClH_{37}NiOP_2$
color	red	violet
cryst size, mm	0.25 × 0.15 × 0.15	0.27 × 0.17 × 0.10
space group	$P2_1/n$	*Pbca*
cell dimens		
a, Å	12.532 (8)	20.638 (5)
b, Å	14.099 (1)	20.09 (1)
c, Å	14.36 (1)	12.913 (5)
β, deg	98.51 (6)	
Z	4	8
V, Å³	2509	5354
D_{calcd}, g cm^{-3}	1.23	1.26
wavelength, Å	0.71069	0.71069
temp, °C	20	20
mol wt	463.681	509.677
linear abs coeff, cm^{-1}	10.61	9.59
2*θ* range, deg	0–50	0–40
unique data	2663	4669
data with [$I \geqslant 3\sigma(I)$]	1958	1277
R(*F*)	0.056	0.056

Table IV. Selected Bond Distances (Å) $\overline{Ni[C(Ph)=C(H)(CO}CH_2SiMe_3)]Cl(PMe_3)_2$ and $\overline{Ni[C(Ph)(PMe_3)C}(H)(COCH_2CMe_2Ph)]Cl(PMe_3)$

	1b		
H(31)–C(3)	0.98 (9)	C(1)–C(3)	1.45 (1)
Ni–Cl	2.298 (3)	C(2)–Si	1.87 (1)
Ni–P(1)	2.191 (3)	Si–C(31)	1.87 (1)
Ni–P(2)	2.189 (3)	Si–C(32)	1.87 (1)
Ni–O(1)	2.535 (7)	Si–C(33)	1.86 (1)
Ni–C(4)	1.896 (7)	C(3)–C(4)	1.34 (1)
P(1)–C(11)	1.83 (1)	C(4)–C(5)	1.48 (1)
P(1)–C(12)	1.78 (1)	C(5)–C(6)	1.37 (1)
P(1)–C(13)	1.81 (1)	C(5)–C(10)	1.40 (1)
P(2)–C(21)	1.81 (1)	C(6)–C(7)	1.38 (1)
P(2)–C(22)	1.81 (1)	C(7)–C(8)	1.36 (1)
P(2)–C(23)	1.79 (1)	C(8)–C(9)	1.36 (1)
O(1)–C(1)	1.24 (1)	C(9)–C(10)	1.38 (1)
C(1)–C(2)	1.50 (1)		
	2		
H(1)–C(1)	0.9 (1)	C(4)–C(5)	1.44 (2)
Ni–Cl	2.266 (4)	C(5)–C(6)	1.31 (2)
Ni–P(1)	2.187 (4)	C(6)–C(7)	1.32 (2)
Ni–C(1)	1.97 (1)	C(7)–C(8)	1.40 (2)
Ni–C(2)	1.94 (1)	O–C(11)	1.24 (1)
P(2)–C(201)	1.79 (1)	C(11)–C(12)	1.51 (2)
P(2)–C(202)	1.82 (1)	C(12)–C(13)	1.59 (2)
P(2)–C(203)	1.80 (1)	C(13)–C(14)	1.53 (2)
P(2)–C(2)	1.76 (1)	C(13)–C(15)	1.52 (2)
P(1)–C(101)	1.81 (2)	C(13)–C(16)	1.52 (2)
P(1)–C(102)	1.77 (2)	C(16)–C(17)	1.40 (2)
P(1)–C(103)	1.85 (2)	C(16)–C(21)	1.37 (2)
C(1)–C(2)	1.44 (2)	C(17)–C(18)	1.43 (2)
C(1)–C(11)	1.44 (2)	C(18)–C(19)	1.30 (3)
C(2)–C(3)	1.51 (2)	C(19)–C(20)	1.37 (2)
C(3)–C(4)	1.38 (2)	C(20)–C(21)	1.36 (2)
C(3)–C(8)	1.41 (2)		

Table V. Selected Bond Angles (deg) for 1b

O(1)–Ni–C(4)	76.8 (3)	O(1)–C(1)–C(3)	121.0 (8)
P(2)–Ni–C(4)	89.5 (3)	O(1)–C(1)–C(2)	120.5 (8)
P(2)–Ni–O(1)	96.6 (2)	C(2)–C(1)–C(3)	118.4 (8)
P(1)–Ni–C(4)	90.5 (2)	C(1)–C(2)–Si	114.3 (6)
P(1)–Ni–O(1)	88.8 (2)	C(2)–Si–C(33)	106.8 (5)
P(1)–Ni–P(2)	174.4 (1)	C(2)–Si–C(32)	110.8 (5)
Cl–Ni–C(4)	177.5 (3)	C(2)–Si–C(31)	109.4 (5)
Cl–Ni–O(1)	105.6 (2)	C(32)–Si–C(33)	108.6 (5)
Cl–Ni–P(2)	90.2 (1)	C(31)–Si–C(33)	111.5 (5)
Cl–Ni–P(1)	89.4 (1)	C(31)–Si–C(32)	109.5 (5)
Ni–P(1)–C(13)	112.7 (4)	C(1)–C(3)–C(4)	121.3 (8)
Ni–P(1)–C(12)	115.2 (4)	Ni–C(4)–C(3)	118.8 (6)
Ni–P(1)–C(11)	120.5 (4)	C(3)–C(4)–C(5)	122.4 (7)
C(12)–P(1)–C(13)	103.5 (6)	Ni–C(4)–C(5)	118.7 (6)
C(11)–P(1)–C(13)	101.4 (5)	C(4)–C(5)–C(10)	121.4 (8)
C(11)–P(1)–C(12)	101.0 (5)	C(4)–C(5)–C(6)	121.8 (7)
Ni–P(2)–C(23)	112.6 (5)	C(6)–C(5)–C(10)	116.7 (8)
Ni–P(2)–C(22)	112.5 (5)	C(5)–C(6)–C(7)	122.3 (9)
Ni–P(2)–C(21)	121.4 (4)	C(6)–C(7)–C(8)	120.0 (9)
C(22)–P(2)–C(23)	106.3 (6)	C(7)–C(8)–C(9)	118.8 (9)
C(21)–P(2)–C(23)	99.4 (6)	C(8)–C(9)–C(10)	121 (1)
C(21)–P(2)–C(22)	102.7 (6)	C(5)–C(10)–C(9)	120.2 (9)
Ni–O(1)–C(1)	101.8 (6)		

it is also appreciably longer than the longest Ni–O separation of 2.004 (8) Å, found in the trimetallic, hydroxo-bridged complex $Ni_3(CH_2C_6H_4\text{-}o\text{-}Me)_4(PMe_3)_2(\mu_3\text{-}OH)_2$, whose structure has been described as consisting of a $Ni(CH_2C_6H_4\text{-}o\text{-}Me)_2$ fragment, stabilized by coordination to the OH groups of the binuclear species $[Ni(CH_2C_6H_4\text{-}o\text{-}Me)(PMe_3)(\mu\text{-}OH)]_2$.[12a] The weakness of this interaction is also manifested by the comparison with the Ni–O separation of 2.229 (5) Å, found in the related chelate system[6] $[\overline{Ni(CH=C(H)C(O)}OEt)(np_3)]^+$. Apart from this apical interaction, the coordination sphere around the nickel atom consists of the four ligands (two phosphorus, one chloride, and the vinylic carbon C(4)) in the basal plane. The two PMe_3 ligands are equivalent and are at an average Ni–P separation of 2.19 (3) Å, while the vinyl carbon exhibits a Ni–C bond distance of 1.896 (7) Å. This length compares well with the value of 1.902 (3) Å found for the analogous distance in the vinyl complex $[Ni(C(CF_3)=C(CF_3)(CH_2C_6H_4NMe_2))(PEt_3)(\mu\text{-}Cl)]_2$;[13] it is intermediate between the 1.84 and 1.95 Å values in the related acyl and alkyl complexes *trans*-$Ni(R)Cl(PMe_3)_2$ (R = $COCH_2SiMe_3$ and CH_2SiMe_3, respectively) and similar to the 1.89 (1) Å value found in the dialkyl $Ni(CH_2SiMe_3)_2(py)_2$.[14] Not unexpectedly, the five atoms Ni, O(1), C(1), C(3), and C(4), composing the metallacyclic unit are almost coplanar, and the conjugated system O(1)–C-

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[12] (a) Carmona, E.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757. (b) Carmona, E.; Paneque, M.; Poveda, M. L.; Rogers, R. D.; Atwood, J. L. *Polyhedron* **1984**, *3*, 317. (c) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524.

[13] Arlen, C.; Pfeffer, M.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1983**, 928.

[14] (a) Carmona, E.; González, F.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1981**, 777. (b) Carmona, E.; González, F.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2108.

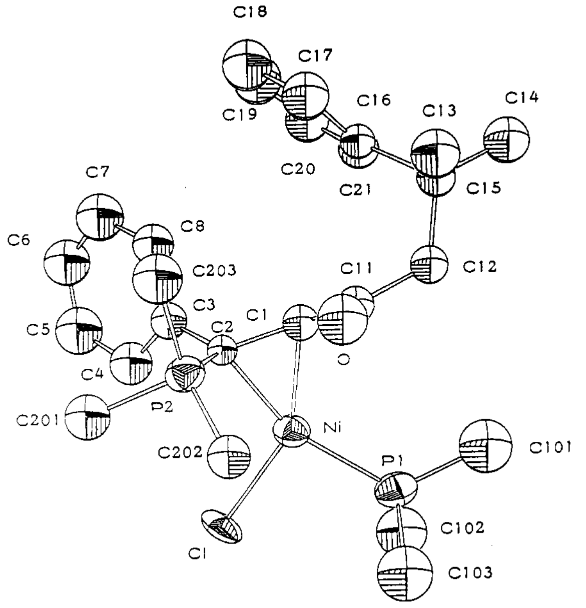


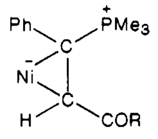
Figure 2. Molecular structure of **2** and atom-labeling scheme.

(1)–C(3)–C(4) eclipses the Ni–C(4) bond vector. The apical Ni–O(1) interaction somewhat lengthens the corresponding C(1)–O(1) bond to 1.25 (1) Å, as compared to the 1.20 (1) Å found in *trans*-Ni(COCH$_2$SiMe$_3$)Cl(PMe$_3$)$_2$,[14b] although conjugation with the C(3)–C(4) double bond may also account for the weakening of the carbonyl linkage. Other bonding parameters defining the vinyl geometry appear normal. For instance, the vinylic C(3)–C(4) bond length of 1.34 (1) Å parallels the corresponding distances in other vinyl complexes of transition metals (e.g. 1.327 Å in (*Z*)-Ni(acac)(PPh$_3$)[C(Ph)=C(Ph)(CH$_3$)],[3a] 1.35 Å in Ni[C(H)=C(H)C(O)OEt](np$_3$)$^+$ [6]).

Formation of the Neophyl Derivative *trans*-(*Z*)-Ni[C(Ph)=C(H)(COCH$_2$CMe$_2$Ph)]Cl(PMe$_3$)$_2$ (1e) and Its Reversible Rearrangement to the Nickelacyclopropane Complex Ni[C(Ph)(PMe$_3$)C(H)(COCH$_2$CMe$_2$Ph)]Cl(PMe$_3$) (2). The Crystal and Molecular Structure of 2. The reaction of PhC≡CH with the neophyl acyl complex *trans*-Ni(COCH$_2$CMe$_2$Ph)Cl(PMe$_3$)$_2$ seems to follow a different course from that described above for other related derivatives, and after the mixture is stirred at room temperature for ca. 24 h, a violet solution (instead of red, as observed for compounds **1a–d**) is obtained. Evaporation of the solvent under vacuum provides a solid residue that can be shown by NMR studies to consist of a mixture of two compounds which can be readily separated by fractional crystallization. The more soluble red material displays physical properties and IR and NMR features (see Tables I and II) very similar to those described above for compounds **1a–d** and can therefore be formulated as *trans*-(*Z*)-Ni[C(Ph)=C(H)(COCH$_2$CMe$_2$Ph)]Cl(PMe$_3$)$_2$- (**1e**). As for the second species, a dark violet product, **2**, analytical data and NMR studies demonstrate it is an isomer of **1e**. The ^{1}H and ^{31}P{^{1}H} NMR spectra of **2** show characteristic NMR signals, very distinct from those of compounds **1**. For example, the resonance corresponding to the vinylic hydrogen atom shifts from δ 6.49 in **1e** to the higher field value of δ 3.0 ppm in **2**. This is consistent with a change in hybridization from sp^2 to sp^3 and indicates that a transformation of the original vinylic ligand has taken place. Furthermore, this hydrogen atom is strongly coupled to one phosphorus nuclei (J_{PH} = 25 Hz). On the other hand, the ^{31}P{^{1}H} NMR of **2** consists of an AX pattern. One of the phosphorus nuclei appears at δ −14.7 ppm, i.e. in the region characteristic of PMe$_3$ bound to nickel, while the other has a chemical shift of 14.6 ppm, indicating the existence in the molecule of **2** of a trimethylphosphonium group.[15] The formation of such a group, that is of an ylidic ligand, is further supported by the appearance of a doublet at δ 1.5 ppm in the ^{1}H NMR spectrum, with a large coupling constant, $^2J_{PH}$ = 14 Hz, characteristic of a phosphonium group.[16] The nickel-bound PMe$_3$ group gives also rise to a doublet, albeit with a smaller coupling constant of 7 Hz. From this data and by comparison with the situation found for other related systems,[17] the existence in the molecule of **2** of a phosphorus ylide ligand of the type VIII can be inferred. Unfortunately, the very low solubility of compound **2** prevents confirmation of this proposal by ^{13}C NMR studies, but nevertheless, good quality crystals of **2** have been obtained and its structure unequivocally determined with the aid of an X-ray study. Figure 2 shows an ORTEP perspective view of **2** including the atom numbering scheme. Relevant structural parameters are presented in Tables III, IV, and VI. If the ylide ligand[18] is considered to formally occupy a single coordination site, the nickel atom is in a distorted trigonal environment. The steric demands of the olefin ligand forces the ClNiP(1) angle to shrink to the rather low value of 93.8 (2)°. The bonding in the nickelacyclopropane unit appears

Table VI. Selected Bond Angles (deg) for 2

C(1)–Ni–C(2)	43.1 (6)	Ni–C(1)–C(11)	110.0 (9)
P(1)–Ni–C(2)	158.8 (4)	Ni–C(1)–C(2)	67.5 (7)
P(1)–Ni–C(1)	117.4 (4)	C(3)–C(4)–C(5)	119 (1)
Cl–Ni–C(2)	105.6 (4)	C(4)–C(5)–C(6)	119 (1)
Cl–Ni–C(1)	148.7 (5)	C(5)–C(6)–C(7)	124 (1)
Cl–Ni–P(1)	93.8 (1)	C(6)–C(7)–C(8)	117 (1)
C(203)–P(2)–C(2)	114.4 (6)	C(3)–C(8)–C(7)	121 (1)
C(202)–P(2)–C(2)	116.6 (6)	C(1)–C(11)–O	122 (1)
C(202)–P(2)–C(203)	108.6 (7)	O–C(11)–C(12)	118 (1)
C(201)–P(2)–C(2)	106.9 (6)	C(1)–C(11)–C(12)	117 (1)
C(201)–P(2)–C(203)	105.2 (7)	C(11)–C(12)–C(13)	114 (1)
C(201)–P(2)–C(202)	103.7 (7)	C(12)–C(13)–C(16)	110 (1)
Ni–P(1)–C(103)	108.2 (6)	C(12)–C(13)–C(15)	108 (1)
Ni–P(1)–C(102)	116.5 (6)	C(12)–C(13)–C(14)	108 (1)
Ni–P(1)–C(101)	122.9 (6)	C(15)–C(13)–C(16)	113 (1)
C(102)–P(1)–C(103)	103.3 (8)	C(14)–C(13)–C(16)	109 (1)
C(101)–P(1)–C(103)	101.2 (8)	C(14)–C(13)–C(15)	107 (1)
C(101)–P(1)–C(102)	102.0 (8)	C(16)–C(21)–C(20)	122 (1)
C(2)–C(1)–C(11)	124 (1)	C(13)–C(16)–C(21)	118 (1)
P(2)–C(2)–C(1)	123.3 (9)	C(13)–C(16)–C(17)	123 (1)
Ni–C(2)–C(1)	69.3 (7)	C(17)–C(16)–C(21)	117 (1)
Ni–C(2)–P(2)	109.4 (6)	C(16)–C(17)–C(18)	118 (1)
C(1)–C(2)–C(3)	115 (1)	C(17)–C(18)–C(19)	119 (1)
P(2)–C(2)–C(3)	110.7 (9)	C(18)–C(19)–C(20)	122 (1)
Ni–C(2)–C(3)	122.7 (9)	C(19)–C(20)–C(21)	119 (1)
C(2)–C(3)–C(8)	119 (1)		
C(2)–C(3)–C(4)	123 (1)		
C(4)–C(3)–C(4)	116 (1)		



VIII

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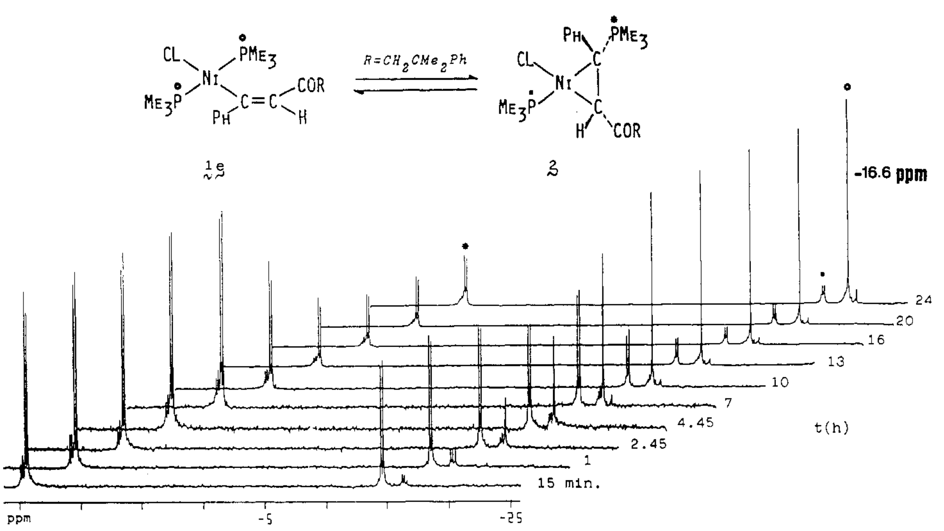
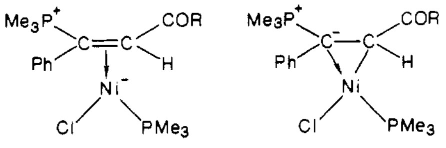


Figure 3. $^{31}P\{^1H\}$ NMR study of the interconversion $2 \rightleftharpoons 1e$.

symmetrical with both Ni–C bond lengths being identical within experimental error (Ni–C(1) = 1.97 (1) Å and Ni–C(2) = 1.95 (2) Å). The α twist of the C(1)–C(2) bond, measured[19] as the angle between the C(1)–C(2) line and the NiClP(1) plane, is 8.5 (7)°, so that C(1) and C(2) deviate by 0.05 and 0.26 Å, respectively, from the mean least-squares coordination plane of the nickel atom. The two Ni–C bond distances compare well not only with those found in nickel(0)–olefin complexes but also with those corresponding to alkyl derivatives of Ni(II) (see above). The geometry of the ylidic ligand exhibits some characteristic features which are worth discussing at this point. The C(1)–C(2) bond of 1.44 (2) Å is shorter than the single bond (1.54 Å) but longer than the double bond length of 1.34 Å, and it is also longer than typical distances in transition metal–ethylene complexes, which are close to ca. 1.40 Å.[20] This C(1)–C(2) distance is similar to the corresponding bond length in the related complex $(C_5H_5)(CO)_2\overline{W[C(H)(PMe_3)C}(H)(COMe)]$[5b] which contains an analogous trimethylphosphonium ylidic ligand. Not surprisingly, the P(2)–C(2) distance at 1.77(1) Å is appreciably greater than the 1.640 (6) Å value found in $CH_2{=}PMe_3$.[21] This probably reflects a larger contribution of the ylide, $=C^-{-}P^+Me_3$, resonance form.[17]

The X-ray data just discussed are in accord with description of the electronic structure of compound 2 in terms of the two limiting forms IX and X. IX corresponds to



IX X

formulation of the complex as a Ni(0) derivative of a cationic olefin ligand. An analogous description has been advanced for the compound $\overline{Ni[CH_2N}(CH_3)_2](PPh_3)Cl$, formulated as a Ni(0) derivative of the iminium cation $H_2C{=}NMe_2^+$.[22] In structure X, complex 2 is considered as a Ni(II) species coordinated to an alkyl carbene ligand, acting formally as a three-electron donor ligand. In both cases, application of electron-counting rules gives a total number of 16 electrons in the valence shell of the metal center.

The X-ray study of complex 2 shows that of the two possible diastereomeric products, the *RR*:*SS* is the preferred one in the solid state. NMR studies (Table I), including selective $^1H\{^{31}P\}$ and other decoupling experiments, show that the solid-state configuration is maintained in solution. For instance, the strong coupling between the Ni–C*H* proton and the ^{31}P nuclei of the phosphonium group, already alluded to, confirms that both occupy a mutually trans position and therefore that diastereomer *RR*:*SS* is the major species in solution. Notwithstanding, minor amounts of the other diastereomer *RS*:*SR* are also present in solution, as suggested by $^{31}P\{^1H\}$ NMR studies. Recently prepared solutions of compound 2, obtained from different crops of crystals, show an accompanying small AX system, with coupling constants and chemical shifts very similar to those found for the main stereoisomer. By careful integration, a stereomer ratio *RR*:*SS*::*RS*:*SR* of ca. 10:1 can be calculated. Upon addition of small amounts of PMe_3 to this mixture, the high-field doublets rapidly broaden and collapse into the base line, at the time that the doublets at ca. 14.6 ppm become singlets. This is clearly due to a rapid, intermolecular exchange between free and Ni-bound PMe_3.

Interconversion of the keto vinyl complex 1e into the isomeric nickelacyclopropane derivative 2 can be observed by NMR, and equilibrated mixtures of these species result when either of the pure isomers is stirred in solution, at room temperature, for ca. 16 h. Figure 3 shows the conversion of 2 into 1e, as followed by $^{31}P\{^1H\}$ NMR spectroscopy. From the equilibrated spectrum a value of 1 ± 0.1 can be calculated for the equilibrium constant, $k_{eq} = [1e]/[2]$. The reverse conversion $1e \rightarrow 2$ is not apparently affected by the presence of free, added PMe_3, and this seems to indicate that the process involves an intramolecular 1,2 PMe_3 shift. This, however, cannot be confirmed since ready decomposition, with formation of $Ni(PMe_3)_4$,

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[19] See: Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, Chapter 37.5 and references therein.

[20] 1.40 (1) Å in *trans*-$Mo(C_2H_4)_2(PMe_3)_4$[20a] and 1.406 (13) Å in $(C_5H_5)_2Nb\ (C_2H_4)Et$.[20b] (a) Carmona, E.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014. (b) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *106*, 5420.

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[23] In IX, the cationic olefinic ligand can be considered a two-electron donor. The $Ni(Cl)PMe_3$ fragment would therefore bear a formal negative charge.

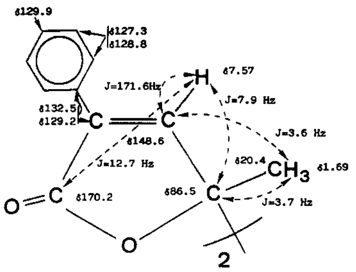
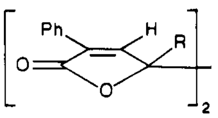


Figure 4. ^1H and $^{13}C\{^1H\}$ NMR data for the butenolide **3a**.

takes place under these conditions. Related, although irreversible, 1,2 phosphine shifts have been observed by others,[5b,e] and in the case of the $Pd[CH{=}CHC(O)OR]X(PPh_3)_2$ compounds,[24] the redistribution is suppressed by PPh_3. The remaining keto alkenyl compounds **1a–d**, show, apparently, no tendency to undergo similar rearrangements. Why these transformations are not observed is a question for which we cannot provide a reasonable answer. We would only like to point out from this respect that the 1,2 phosphine shift has only been observed for the less electron donating of the alkyl groups studied. Apparently in agreement with that, we have detected recently a similar behavior for the benzyl group, $CH_2C_6H_5$. Work aimed at characterizing the products of this reaction is under way.

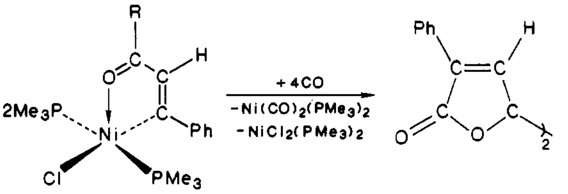
Reaction of the Keto Vinyl Complexes 1a–e with CO. Formation of α,β-Butenolides 3. Upon exposure of diethyl ether solutions of the vinyl compounds **1** to carbon monoxide, formation of white, microcrystalline solids is gradually observed. When crystallization of these products is complete, the mother liquor can be shown by IR and ^{31}P NMR studies to consist of an equimolar mixture of $Ni(CO)_2(PMe_3)_2$ and $NiCl_2(PMe_3)_2$, as the only metal-containing products. The white materials **3a–e** are insoluble in acetone, ethanol, and chloroform but can be recrystallized from Et_2O or CH_2Cl_2–Et_2O mixtures. Microanalytical and mass spectral data as well as IR and NMR data are collected in Tables A and B of the supplementary material. ^1H and ^{13}C NMR data for a representative member of this series of compounds, **3a**, R = CH_3, are shown schematically in Figure 4. The presence of an ester functionality in the molecules of **3** is manifested by the appearance of a strong absorption at ca. 1750 cm^{-1}, while the C=C bond of the five-membered butenolide ring and the phenyl group are respectively responsible for the absorptions at 1495 (C=C) and 3000 and 1580 cm^{-1}. From these and other data, compounds **3** can be formulated as dimers of γ-but-2-enolactone, with the structure indicated in XI. This has been confirmed by an X-ray study, to be



XI

reported independently,[25] carried out with the methyl derivative **3a**. Although two different stereomers may in principle form, only one isomer can be detected by NMR studies. However, in the case of **3a**, very small amounts of a minor stereomer can, sometimes, be obtained. X-ray studies[25] reveal the major and minor stereomers of **3a** correspond respectively to the racemic and meso forms.

The formation of the α,β-butenolide dimers can be represented as shown in eq 2.



(2)

Although the carbonylation reaction is essentially quantitative by NMR, yields of isolated α,β-butenolides range between 50 and 80% due to difficulties in their sepparation from the other reaction products. Dimers of α,β-butenolides are formed as byproducts in some carbonylations of organic halides in the presence of alkynes, induced or catalyzed by $Ni(CO)_4$.[26] An analogous reaction of β-bromostyrene with $Ni(CO)_4$ and alkynes, in dimethylformamide at 60 °C, produces α,β-butenolides in moderate yields.[4a] In general, carbonylations of organic halides, RX, based on $Ni(CO)_4$, are difficult to carry out when R is a normal alkyl group.[27] Therefore, the synthetic procedure described in this paper provides a simple route to α,β-butenolides which are difficult to prepare otherwise.

Rather interestingly, the butenolide dimers can be obtained, in a one-pot synthesis, by reaction of the alkyls *trans*-$Ni(Cl)R(PMe_3)_2$, with CO and $PhC{\equiv}CH$ plus CO, successively. The parent alkyls required for this transformation can be readily prepared, starting from $NiCl_2(PMe_3)_2$, by conventional Grignard routes[28] and need not be isolated as pure solids. The carbonylation reaction, which afford the corresponding acyls, can be accomplished with the petroleum ether solutions which result after workup of the alkylation reactions. Since these acyls do not react further with CO, the addition of $PhC{\equiv}CH$ and the second carbonylation can be carried out simultaneously (eq 3). According to the stoichiometry of the reaction, as

$$\mathrm{Ni(Cl)R(PMe_3)_2} \xrightarrow{\mathrm{CO}} \xrightarrow{\mathrm{PhC{\equiv}CH,\ CO}} [\overline{\mathrm{CH{=}C(Ph)C(O)OC}}\mathrm{(R)}-]_2 \quad (3)$$

depicted in eq 2, half of the starting $NiCl_2(PMe_3)_2$ can theoretically be recovered, and the carbonyl $Ni(CO)_2(PMe_3)_2$ may also be recycled.[29] A possible reaction pathway for the formation of these products is shown in Scheme III. Carbonylation of the keto vinyl complexes **1** could induce elimination of the organic fragment in A, by means of C–O bond formation and nickel migration. This could yield a short-lived species, B, which could undergo homolytic cleavage of the Ni–C bond, with formation of allylic radicals that would couple to the dimeric α,β-butenolides. The resulting Ni(I) complex $NiCl(PMe_3)_3$ would in turn disproportionate readily, under CO, to the observed inorganic complexes $Ni(CO)_2(PMe_3)_2$ and $NiCl_2(PMe_3)_2$.[30] Attempts have been made to obtain monomeric α,β-butenolides by carrying out the final carbonylation in the presence of KOH, ROH, or Ph_2NH, but so far without success.

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[24] Rybin, L. V.; Petrovskaya, E. A.; Rubinskaya, M. I.; Kuz'mina, L. G.; Struchkov, Yu. T.; Kaverin, V. V.; Koneva, N. Yu. *J. Organomet. Chem.* **1985**, *288*, 119.

[25] Gutièrrez-Puebla, E.; Monge, A.; Ruiz, C., to be submitted for publication.

[26] Chiusoli, G. P.; Cassar, L. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 124.

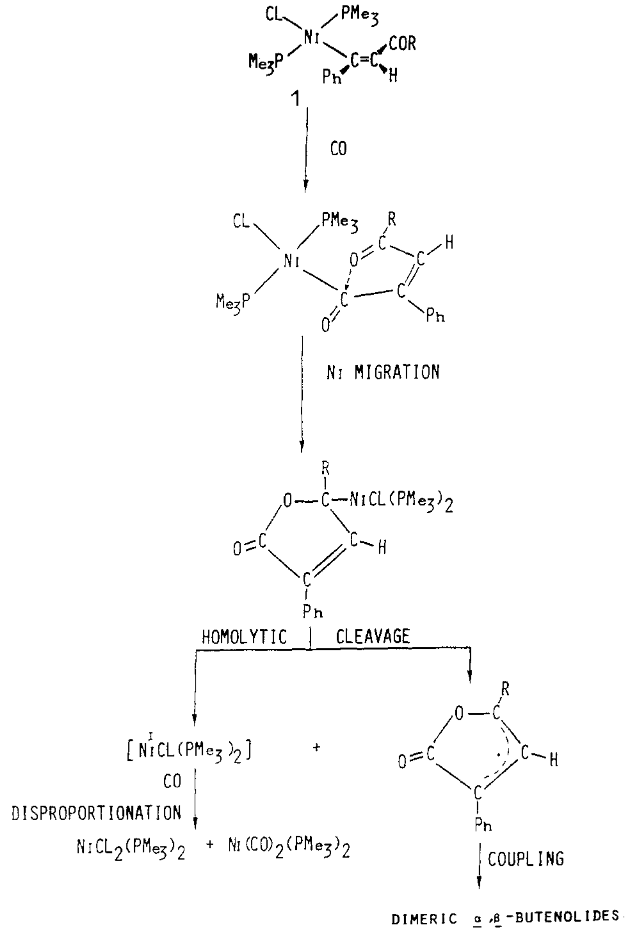
[27] Organic halides, RX, can only be efficiently carbonylated by $Ni(CO)_4$ when R is an allyl, vinyl, or an activated alkyl group such as benzyl. See: Jolly, P. W.; Wilke, G. In *The Organic Chemistry of Nickel*; Academic Press: New York, 1975; Vol. II (Organic Synthesis).

[28] See ref 12 for the preparation of $Ni(CH_2C_6H_4\text{-}o\text{-}Me)Cl(PMe_3)_2$.

[29] Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2515.

[30] Although some $NiCl(PR_3)_3$ complexes are known, the PMe_3 derivative is very unstable toward disproportionation to $NiCl_2(PMe_3)_2$ and $Ni(PMe_3)_4$. See: Bartsch, E.; Dinjus, E.; Fischer, R.; Uhlig, E. *Z. Anorg. Allg. Chem.* **1977**, *433*, 5.

Scheme III



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 (C_6D_6) 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 boiling point of 40–60 °C. The compounds PMe_3[31] and $NiCl_2(PMe_3)_2$[32] and the acyls $Ni(COR)Cl(PMe_3)_2$ (R = Me,[12c] CH_2SiMe_3,[14b] CH_2CMe_3,[12b] $CH_2C_6H_4$-*o*-Me,[12a] CH_2CMe_2Ph[14b]) were prepared according to literature methods.

Preparation of the Keto Vinyl Complexes *trans*-(*Z*)-$Ni[C(Ph)=C(H)(COR)]Cl(PMe_3)_2$ (1a–e) and Rearrangement of the Neophyl Derivative 1e into the Nickelacyclopropane Complex $Ni[C(Ph)(PMe_3)C(H)(COCH_2CMe_2Ph)]Cl(PMe_3)$ (2). The vinyl compounds **1a–e** can be prepared by insertion of PhC≡CH into the nickel–carbon bond of the corresponding acyls *trans*-$Ni(COR)Cl(PMe_3)_2$, using diethyl ether or a ca. 2:1 Et_2O–acetone mixture as the solvent. A detailed synthesis for the (trimethylsilyl)methyl derivative **1b** is given below.

To a stirred solution of the acyl $Ni(COCH_2SiMe_3)Cl(PMe_3)_2$ (0.54 g, ca. 1.5 mmol) in 25 mL of Et_2O (or Et_2O–acetone) is added an excess of phenylacetylene (0.2 mL, ca. 2 mmol). The mixture is stirred overnight at 20 °C and the solvent removed in vacuo. Extraction with Et_2O (30 mL), centrifugation, partial removal of the solvent in vacuo, and cooling at −30 °C for several hours provide red crystals of the desired product in ca. 50% yield.

Table VII. Fractional Coordinates for 1b

atom	*x*/*a*	*y*/*b*	*z*/*C*
H(31)	0.093 (8)	0.228 (7)	−0.069 (7)
Ni	0.33680 (9)	0.18840 (8)	0.10960 (7)
Cl	0.4659 (2)	0.2004 (2)	0.2406 (1)
P(1)	0.4254 (2)	0.2929 (2)	0.0379 (2)
C(11)	0.3660 (9)	0.3421 (8)	−0.0765 (8)
C(12)	0.553 (1)	0.2545 (9)	0.0127 (9)
C(13)	0.456 (1)	0.3999 (9)	0.1066 (8)
P(2)	0.2582 (2)	0.0734 (2)	0.1762 (2)
C(21)	0.1271 (9)	0.0285 (8)	0.1251 (8)
C(22)	0.339 (1)	−0.033 (1)	0.191 (1)
C(23)	0.229 (1)	0.104 (1)	0.291 (1)
O(1)	0.1984 (5)	0.3153 (5)	0.1288 (4)
C(1)	0.1334 (7)	0.3061 (7)	0.0549 (7)
C(2)	0.0360 (7)	0.3691 (6)	0.0355 (6)
Si	−0.0874 (2)	0.3207 (2)	0.0776 (2)
C(31)	−0.1383 (9)	0.2162 (8)	0.0037 (8)
C(32)	−0.056 (1)	0.2837 (9)	0.2043 (9)
C(33)	−0.1886 (9)	0.4187 (8)	0.0674 (8)
C(3)	0.1489 (7)	0.2334 (6)	−0.0140 (6)
C(4)	0.2339 (6)	0.1742 (6)	−0.0004 (5)
C(5)	0.2515 (7)	0.0995 (6)	−0.0694 (5)
C(6)	0.3486 (7)	0.0527 (6)	−0.0651 (6)
C(7)	0.3654 (8)	−0.0182 (7)	−0.1279 (7)
C(8)	0.2838 (9)	−0.0447 (7)	−0.1968 (7)
C(9)	0.1862 (9)	−0.0011 (9)	−0.2014 (7)
C(10)	0.1689 (8)	0.0713 (8)	−0.1406 (7)

Compounds **1a**, **1c**, and **1d** can be prepared similarly.

The neophyl complex **1e** is obtained from $Ni(COCH_2CMe_2Ph)Cl(PMe_3)_2$ (0.4 g, 1 mmol) and PhC≡CH, as indicated above. After being stirred for ca. 24 h, the reaction mixture is evaporated to dryness and the residue extracted with 75 mL of Et_2O, whereupon a deep red-purple solution is obtained. Centrifugation and cooling at −30 °C overnight provides dark violet crystals of **2** (0.13 g, ca. 25%). Evaporation of the mother liquor to ca. 5 mL and cooling at −30 °C furnish red crystals of **1e** in ca. 30% yield.

Synthesis of the γ-But-2-enolactone Dimers 3. (a) By Carbonylation of the Vinyl Complexes 1. A solution of the complex $Ni[C(Ph)=C(H)(COCH_2CMe_2Ph)]Cl(PMe_3)_2$ (**1e**) (0.23 g, 0.45 mmol) in diethyl ether (15 mL) is reacted with CO at ambient temperature and pressure. After being stirred for a few minutes, the solution becomes red and a white solid forms. The mixture is stirred for 24 h and then cooled at −30 °C. Filtration provides 0.106 g (80% yield) of the corresponding α,β-butenolide (2-phenyl-4-neophyl-γ-but-2-enolactone dimer, **3e**). The mother liquor is concentrated to ca. 5 mL and cooled at −30 °C to provide 0.06 g of $NiCl_2(PMe_3)_2$. The supernatant is evaporated to dryness and dissolved in 0.5 mL of C_6D_6. NMR studies show the presence of $Ni(CO)_2(PMe_3)_2$ as the major product, together with small amounts of the butenolide **3e**. A similar reaction carried out in a sealed NMR tube shows the carbonylation process to be quantitative by NMR.

Compound **3e** is insoluble in ethanol, acetone, and benzene, partially soluble in Et_2O, and very soluble in CH_2Cl_2. Recrystallization from Et_2O–CH_2Cl_2 mixtures affords crystals of analytical purity. The remaining butenolides prepared in this work can be obtained likewise, starting from the corresponding keto vinyl complexes **1**. The carbonylations are also quantitative by NMR, but yields of isolated α,β-butenolides vary between 50 and 80% due to differences in solubility and hence in the facility with which they can be separated from the other products of the reaction. The lowest yield of isolated product corresponds to compound **3a**, which is the most soluble in diethyl ether.

(b) Starting from $Ni(Cl)R(PMe_3)_2$. The alkyl derivatives can be prepared by reacting a suspension of $NiCl_2(PMe_3)_2$ (0.56 g, 2 mmol) in Et_2O (40 mL) with the Grignard reagent Mg(R)Cl (or in the case of the *o*-methylbenzyl complex, by the oxydative addition of Me-*o*-$C_6H_4CH_2Cl$ (0.26 mL, 2 mmol) to $Ni(cod)_2$ (0.55 g, 2 mmol) in the presence of PMe_3 (0.4 mL, 4 mmol)) as previously described.[12,14] When the alkylation reaction is complete, the solvent is removed under vacuum and the residue extracted with petroleum ether (40 mL). Carbon monoxide is then bubbled through the resulting solution for ca. 5 min, producing yellow

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(31) Wolfsberger, W.; Schmidbauer, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.

(32) Dahl, O. *Acta Chem. Scand.* **1969**, *23*, 2342.

Table VIII. Fractional Coordinates for 2

atom	x/a	y/b	z/c
H(1)	0.377 (7)	0.194 (7)	0.32 (1)
Ni	0.36680 (9)	0.07800 (9)	0.3128 (1)
Cl	0.3026 (2)	−0.0053 (2)	0.2538 (3)
P(2)	0.2773 (2)	0.0968 (2)	0.4971 (3)
C(201)	0.1969 (7)	0.0705 (8)	0.463 (1)
C(202)	0.3174 (7)	0.0200 (7)	0.536 (1)
C(203)	0.2675 (8)	0.1489 (8)	0.609 (1)
P(1)	0.4566 (2)	0.0285 (2)	0.2662 (3)
C(101)	0.5363 (9)	0.0638 (9)	0.289 (1)
C(102)	0.4624 (9)	0.0039 (9)	0.134 (1)
C(103)	0.4626 (9)	−0.051 (1)	0.337 (1)
C(1)	0.3745 (7)	0.1646 (7)	0.383 (1)
C(2)	0.3095 (6)	0.1382 (6)	0.3877 (9)
C(3)	0.2577 (7)	0.1795 (7)	0.334 (1)
C(4)	0.2197 (8)	0.1563 (7)	0.253 (1)
C(5)	0.1688 (9)	0.1980 (9)	0.213 (1)
C(6)	0.1596 (8)	0.2575 (9)	0.252 (2)
C(7)	0.1947 (8)	0.2838 (9)	0.328 (1)
C(8)	0.2450 (7)	0.2450 (8)	0.370 (1)
O	0.4090 (5)	0.1310 (5)	0.5500 (7)
C(11)	0.4209 (6)	0.1600 (7)	0.167 (1)
C(12)	0.4837 (6)	0.1985 (7)	0.456 (1)
C(13)	0.4847 (6)	0.2672 (7)	0.518 (1)
C(14)	0.5502 (8)	0.3010 (8)	0.497 (1)
C(15)	0.4808 (8)	0.2519 (8)	0.633 (1)
C(16)	0.4303 (6)	0.3124 (6)	0.480 (1)
C(7)	0.3802 (8)	0.3362 (8)	0.544 (1)
C(18)	0.3319 (8)	0.3793 (9)	0.501 (2)
C(19)	0.3352 (9)	0.3962 (9)	0.403 (1)
C(20)	0.3842 (8)	0.3748 (8)	0.339 (1)
C(21)	0.4311 (7)	0.3338 (8)	0.379 (1)

microcrystals of the acyls $Ni(COR)Cl(PMe_3)_2$, which are redissolved in Et_2O–acetone. Phenylacetylene (ca. 3 mmol) is added and the mixture stirred, under CO, overnight. The solvent is removed in vacuo, ethanol (15 mL) added, and the flask cooled at −30 °C for 2–3 h. White crystals of the butenolides **3a–e** are obtained in ca. 20% yield based on the starting $NiCl_2(PMe_3)_2$.

Crystallographic Studies. The air sensitive crystals of **1b** and **2** were mounted in glass capillaries under nitrogen atmosphere and mounted on the goniometer head. Diffraction intensity data were collected on an Enraf-Nonius CAD-4F diffractometer with graphite–monochromated Mo Kα radiation (λ = 0.71069 Å), using the ω–2θ scan technique. For **1b**, 2663 independent reflections were measured in a quadrant, with $0 < \theta < 25°$; 1958 reflections were considered observed ($I > 3\sigma(I)$) after data reduction. For **2**, of the 4669 reflections measured in an octant out to $2\theta = 40°$, 1277 unique reflections were considered observed ($I > 3\sigma(I)$). The intensity standards were stable within ±7% and ±6%, respectively, throughout data collection. The structures were solved by Patterson and Fourier techniques and refined (183 and 148 variables, respectively) by least squares to an R value of 5.6 in both cases. An absorption correction was not applied for **1b** or **2**. The carbon atoms in **2** were considered isotropic, as well as the methyl carbon atoms attached to P(1), P(2), and Si in **1b**. The hydrogen atoms were geometrically placed and included in the refinement with fixed contributions, except for H(31) in **1b** and H(1) in **2**, whose coordinates were taken from a Fourier difference map and refined. All computations during data reduction and structure solution and refinement were carried out with the X-RAY system. The Fractional coordinates for **1b** and **2** are reported in Tables VII and VIII.

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Registry No. **1a**, 90968-85-7; **1b**, 90990-47-9; **1c**, 90968-86-8; **1d**, 119273-18-6; **1e**, 90989-37-0; **2**, 90990-48-0; **3a**, 119245-43-1; **3b**, 119245-44-2; **3c**, 119245-45-3; **3d**, 119245-46-4; **3e**, 119245-47-5; *trans*-$Ni(COCH_3)Cl(PMe_3)_2$, 42481-73-2; *trans*-$Ni(COCH_2SiMe_3)Cl(PMe_3)_2$, 75982-73-9; *trans*-$Ni(COCH_2CMe_3)Cl(PMe_3)_2$, 90896-43-8; *trans*-$Ni(COCH_2C_6H_4$-*o*-$Me)Cl(PMe_3)_2$, 98170-39-9; *trans*-$Ni(COCH_2CMe_2Ph)Cl(PMe_3)_2$, 75982-78-4; $PhC\equiv CH$, 536-74-3; $NiCl_2(PMe_3)_2$, 20087-67-6; $Mg(Me)Cl$, 676-58-4; $Mg(CH_2SiMe_3)Cl$, 13170-43-9; $Mg(CH_2CMe_3)Cl$, 13132-23-5; Me-*o*-C_6H_4-CH_2Cl, 552-45-4; $Mg(CH_2CMe_2Ph)Cl$, 35293-35-7; $Ni(cod)_2$, 1295-35-8.

Supplementary Material Available: Tables of ^1H NMR, IR, and ^{13}C NMR data and elemental analyses for compounds **3** (Tables A and B) and tables of additional bond distances and angles (Tables C–E) and fractional coordinates for the H atoms of and thermal parameters for **1b** and **2** (Tables F–I) (9 pages); listings of observed and calculated structure factors for **1b** and **2** (Tables J and K) (50 pages). Ordering information is given in any current masthead page.