Reaction of nickel(O) with .alpha.-keto phosphonates. Syntheses, characterization, and x-ray crystal structure of (PPh3)2Ni(.eta.2-(CO)RC(O)P(O)(OMe)2)

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solution refluxed for 80 min. Removal of the solvents in vacuo afforded an oil, which was dissolved in 10 mL of EtOH and then treated with $NaBPh_4$ (0.068 g, 0.20 mmol) also in 10 mL of EtOH. Addition of *n*-pentane induced precipitation of the product (0.070 g, 34%).

$[Pt(NC_9H_6CO)(1,5\text{-}COD)](CF_3SO_3)$. $PtCl_2(1,5\text{-}COD)$ (0.10 g, 0.30 mmol) was dissolved in 2 mL of 1:1 $EtOH/CH_2Cl_2$ and then treated with a solution of $Ag(CF_3SO_3)$ (0.15 g, 0.60 mmol) in 1 mL of EtOH. Stirring of the suspension at room temperature for 60 min and then cooling to −20 °C was followed by filtration through Celite into a precooled (−20 °C) solution of 1 (0.084 g, 0.60 mmol) in 2 mL of EtOH. The precipitate that formed was immediately filtered (under nitrogen) and dried to afford the product (0.12 g, 65%). Anal. Calcd for $C_{19}H_{18}NF_3O_4PtS$: C, 37.50; H, 2.98; N, 2.30. Found: C, 37.05; H, 2.93; N, 2.61.

The kinetics for the cationic complexes were measured by using ^{31}P NMR spectroscopy ($c_0 = 3.3 \times 10^{-2}$ M with $O \leftarrow PPh_3$ as the reference in a $CDCl_3$ capillary). Typically, *cis*-$PtCl_2L_2$ (0.1 mmol) was dissolved in 1 mL of 1:1 acetone/CD_2Cl_2. Addition of $Ag(CF_3SO_3)$ (0.025 g, 0.10 mmol) in 0.5 mL of acetone gave a suspension, which was stirred for 30 min. Cooling to −60 °C was followed by filtration over Celite into a precooled (−60 °C) solution of 1 (16 mg, 0.10 mmol) in 1 mL of CD_2Cl_2. A ^{31}P spectrum was measured at −60 °C; the sample was shaken at room temperature for 15 min, recooled to −60 °C, at which temperature there is little or no reaction, and then monitored via ^{31}P NMR spectroscopy. A plot of ln $(c_0 - c_t)$ vs t for L = PEt_3 is shown in Figure 2.

Quinoline-8-carboxaldehyde-*d*. 8-Bromoquinoline (2.66 g, 12.8 mmol) was dissolved in 12 mL of THF and the solution cooled to −78 °C. Treatment with 1.5 equiv of butyllithium (9.2 mL of a 2 M solution) in hexane and stirring for 10 min at −78 °C was followed by fast addition of 1.2 mL of DMF-d_7. Warming to room temperature and destroying excess butyllithium with acid was followed by extraction with ether. This removes nonbasic organic impurities. The aqueous solution was then made basic and once again extracted with ether. Drying of this second ether layer was followed by concentration in vacuo to afford the crude product, which was recrystallized from water (890 mg, 45%; 99.2% D labeled). ^2H NMR: δ = 11.5 (CDO). ^{13}C NMR: δ = 192.5 (CDO, $^1J(^{13}C,^2H)$ = 28.7 Hz).

Preparation of $[Pt(\mu\text{-}Cl)(NC_9H_6CO)]_2$. The π-allyl dimer $[Pt(\mu\text{-}Cl)\{CH_2C(CH_3)CH_2\}]_2$ (25 mg, 0.04 mmol) was dissolved in 1 mL of CH_2Cl_2. Solid quinoline-8-carboxaldehyde (13.8 mg, 0.08 mmol) was added to this solution, with the result that a red-brown precipitate immediately formed (27.5 mg, 89%). Anal. Calcd for $C_{20}H_{12}H_2O_2Cl_2Pt_2$: C, 31.06; H, 1.56; N, 3.62; Cl, 9.17. Found: C, 30.35; H, 1.58; N, 3.54; Cl, 9.16.

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Supplementary Material Available: Partial NMR spectra of 1 and *trans*-$PtCl_2(1)(PEt_3)$ and NMR spectra showing the disappearance of **3a** and the development of **4a** (2 pages). Ordering information is given on any current masthead page.

Reaction of Nickel(0) with α-Keto Phosphonates. Syntheses, Characterization, and X-ray Crystal Structure of $(PPh_3)_2Ni(\eta^2\text{-}(CO)RC(O)P(O)(OMe)_2)$

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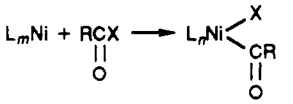
Reaction of Ni(1,5-cyclooctadiene)$_2$ with α-keto phosphonates in the presence of PPh_3 affords $(PPh_3)_2Ni(\eta^2\text{-}(CO)RC(O)P(O)(OMe)_2)$ (R = phenyl, **1**; *p*-tolyl, **2**; *p*-chlorophenyl, **3**; methyl, **4**; ethyl, **5**), characterized by IR, ^1H NMR, and ^{31}P NMR spectra. The single-crystal X-ray diffraction of **5** [monoclinic, $P2_1/n$, a = 9.640 (3), b = 18.910 (8), c = 20.821 (8) Å, β = 90.03 (3)°, V = 3796 (2) Å^3, Z = 4, R_1 = 0.049] has revealed that ethyl keto phosphonates coordinate to the $Ni(PPh_3)_2$ moiety in an η^2-CO mode, making the Ni geometry square planar. These complexes undergo exchange reaction of α-keto phosphonate ligand in solution. Judging from the π-coordination ability of α-keto phosphonates toward Ni(0), a $P(O)(OMe)_2$ group has been estimated to be electronegative by as much as a CF_3 group.

Introduction

Zerovalent nickel complexes are very reactive toward many organic compounds. Especially, the reaction with organic compounds containing acyl groups (RC(O)Z) is interesting because the reaction pattern depends on the substituent (Z) on the acyl carbon. Acyl halides (Z = halogen) undergo oxidative addition to give (acyl)(halide)nickel complexes (eq 1).[4] Carboxylic esters (Z = OR′)



$$L_mNi + \underset{\underset{O}{\|}}{RCX} \longrightarrow L_nNi\genfrac{}{}{0pt}{}{\diagup X}{\diagdown \underset{\underset{O}{\|}}{CR}} \qquad (1)$$

undergo either oxidative addition at the RCO–OR′ bond to a Ni(0) complex to give an (acyl)(alkoxy or aryloxy)-nickel complex (eq 2) or oxidative addition at the RCOO–R′ bond to give a (carboxylato)(alkyl or aryl)nickel complex

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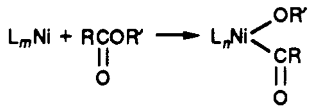
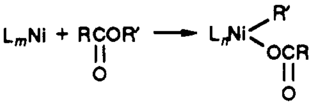
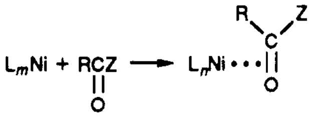


(2)



(3)

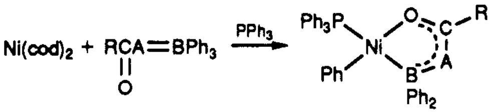
(eq 3).[5] The mode of the scission of the carboxylic ester bond depends on the ester employed and the ligand coordinated to nickel. Aldehydes (Z = H),[6] ketones (Z = R′),[7] keto esters (Z = COOR′),[7b] and acyl cyanides (Z = CN)[7b,8] react with a Ni(0) complex to give an η^2-(CO) complex (eq 4).



(4)

Z = H, R′, COOR′, CN

In 1986, a unique reaction was reported that α-ketoylides, RC(O)—A═BPh$_3$, of phosphorus and arsenic (A = CR′, N; B = P, As) react with a Ni(0) complex to yield a P O or As O chelated complex as described in eq 5.[9]



(5)

A = CR′, N; B = P, As

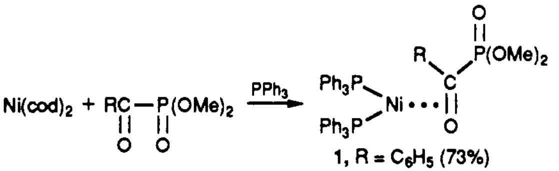
According to the above results, it can be said that acyl carbon–halogen and -oxygen bonds are susceptible to oxidative addition toward zerovalent nickel, while acyl carbon–hydrogen, -alkyl carbon, -aryl carbon, -keto ester carbon, -cyanide carbon, ylide carbon, and ylide nitrogen bonds are not cleaved on reaction with Ni(0) complexes. Though many acyl compounds have been examined, the reaction of organic compounds containing an acyl carbon–phosphorus bond with a zerovalent nickel complex has not been reported so far.

Recently we found that α-keto phosphonates, RC(O)P(O)(OR′)$_2$, having a covalent bond between an acyl carbon and a pentavelent phosphorus, undergo decarbonylation catalyzed by a Pd complex to give phosphonates, RP(O)(OR′)$_2$, where the acyl carbon–P bond is activated.[10] In this paper we report the reaction of α-keto phosphonates with a zerovalent nickel complex.

Results and Discussion

Syntheses of (PPh$_3$)$_2$Ni(η^2-(CO)-α-keto phosphonates). We chose Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) as a nickel(0) complex source because a cod ligand is known to be readily released from the complex to provide an active site on a zerovalent nickel atom. Ni(cod)$_2$ and 2 times the molar amount of PPh$_3$ were suspended in a small amount of Et$_2$O, and then 3 times the molar amount of α-keto phosphonate was added to the heterogeneous solution at room temperature. After being stirred for several minutes, the solution became homogeneous. Continuing stirring for further several minutes to 2 days depending upon α-keto phosphonates at room temperature led to the formation of yellow or yellowish orange precipitates in fairly good yield.

The isolated complexes have the structure in which Ni atom has two PPh$_3$ and RC(O)P(O)(OMe)$_2$ coordinating to Ni through the C═O π bond (eq 6). The structure was deduced from the spectroscopic data and confirmed by the X-ray structural analysis described later. These complexes gradually decompose on exposure to air.



(6)

1, R = C$_6$H$_5$ (73%)
2, R = *p*-MeC$_6$H$_4$ (72%)
3, R = *p*-ClC$_6$H$_4$ (65%)
4, R = CH$_3$ (79%)
5, R = CH$_3$CH$_2$ (89%)

Spectroscopic Data. The IR, ^{1}H NMR, and ^{31}P{^{1}H} NMR data of 1–5, together with the free α-keto phosphonates, are summarized in Table I. In IR spectra, free α-keto phosphonates show ν_{CO} bands at 1654–1659 cm^{-1} for aryl keto phosphonates and at 1702 cm^{-1} for alkyl keto phosphonates. In contrast, the ν_{CO} band of the nickel complexes was not observed in the normal ν_{CO} region. The new absorption due to ν_{CO} has not been assigned. A similar disappearance of ν_{CO} in the IR spectrum upon coordination to nickel(0) through a C═O π-bond has been reported for (PEt$_3$)$_2$Ni(PhCOPh)[7e] and (*t*-BuNC)$_2$Ni(π-diethyl keto malonate).[7b]

There are two $\nu_{P=O}$ bands in the range 1262–1275 cm^{-1} for the free aryl keto phosphonates, presumably due to Fermi resonance,[11] while there is one $\nu_{P=O}$ band at 1264 cm^{-1} for the free alkyl keto phosphonates. The nickel complexes have two ν_{PO} bands in the range 1229–1261 cm^{-1}, which are 20–30 cm^{-1} lower than those for the corresponding free α-keto phosphonates. Ittel reported with (*t*-BuNC)$_2$Ni(η^2-(CO)diethyl keto malonate) that the ν_{CO} bands attributable to the carbethoxy groups not coordinating to Ni are shifted from 1760 and 1735 cm^{-1} for the free ligand to 1730 and 1710 cm^{-1} in the complex.[7b] Therefore, the lowering of ν_{YO} for compounds containing a -C(O)Y(O)- moiety by C═O π-coordination to a zerovalent transition metal seems to be a general trend irrespective of the kind of Y (Y = C, P). As mentioned below, the X-ray structural analysis of (PPh$_3$)$_2$Ni(η^2-(CO)EtC(O)P(O)(OMe)$_2$) revealed that there is a weak interaction between the Ni and the phosphoryl oxygen. The weak coordination may also cause the lowering of ν_{CO} to some extent in our system.

In ^{1}H NMR, the OMe groups in the free α-keto phosphonates exhibit one doublet at about 3.8 ppm. In contrast, the corresponding resonances in the complexes show two doublets at about 3.4 and 3.7 ppm. If the rigid structure of the complex exhibited by X-ray analysis (vide infra) is kept in solution, the two OMe groups are magnetically different. However, even if the structure is not frozen in a solution, in other words, if a P–C bond rotation and/or a propeller-like movement about the Ni–(π-C═O)

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Table I. IR, ^{1}H NMR, and ^{31}P{^{1}H} NMR Data

compound	IR,^{a} cm^{-1}		^{1}H NMR,^{b} δ	^{31}P{^{1}H} NMR,^{c} δ
	ν_{CO}	ν_{PO}		
$C_6H_5C(O)P(O)(OMe)_2$	1659	1275 1262	3.84 (d, J = 10.6 Hz, 6 H, OCH_3) 7.4–8.2 (m, 5 H, C_6H_5)	−0.42 (s)
p-$MeC_6H_4C(O)P(O)(OMe)_2$	1654	1274 1262	2.43 (s, 3 H, $C_6H_4CH_3$) 3.84 (d, J = 10.4 Hz, 6 H, OCH_3) 7.2–8.2 (m, 4 H, C_6H_4)	−0.20 (s)
p-$ClC_6H_4C(O)P(O)(OMe)_2$	1656	1275 1265	3.85 (d, J = 10.8 Hz, 6 H, OCH_3) 7.4–8.3 (m, 4 H, C_6H_4)	−0.90 (s)
$MeC(O)P(O)(OMe)_2$	1702	1264	2.38 (d, J = 6.0 Hz, 3 H, $C(O)CH_3$) 3.76 (d, J = 10.8 Hz, 6 H, OCH_3)	−1.80 (s)
$EtC(O)P(O)(OMe)_2$	1702	1264	1.08 (t, J = 7.0 Hz, 3 H, CH_2CH_3) 2.80 (q, J = 7.0 Hz, 2 H, CH_2CH_3) 3.80 (d, J = 10.2 Hz, 6 H, OCH_3)	−1.60 (s)
$(PPh_3)_2Ni(C_6H_5C(O)P(O)(OMe)_2)$ (1)		1252 1240	3.36 (d, J = 10.8 Hz, 3 H, OCH_3) 3.71 (d, J = 10.2 Hz, 3 H, OCH_3) 6.9–7.7 (m, 35 H, C_6H_5)	18.59 (dd, J = 7.4, 4.9 Hz) 31.31 (dd, J = 34.1, 4.9 Hz) 37.03 (dd, J = 34.1, 7.4 Hz)
$(PPh_3)_2Ni(p$-$CH_3C_6H_4C(O)P(O)(OMe)_2)$ (2)		1254 1239	2.02 (s, 3 H, $CH_3C_6H_4$) 3.35 (d, J = 10.8 Hz, 3 H, OCH_3) 3.69 (d, J = 10.2 Hz, 3 H, OCH_3) 6.9–7.7 (m, 35 H, C_6H_5)	18.47 (dd, J = 9.0, 5.5 Hz) 31.25 (dd, J = 34.5, 5.5 Hz) 36.99 (dd, J = 34.5, 9.0 Hz)
$(PPh_3)_2Ni(p$-$ClC_6H_4C(O)P(O)(OMe)_2)$ (3)		1254 1238	3.41 (d, J = 10.2 Hz, 3 H, OCH_3) 3.74 (d, J = 9.6 Hz, 3 H, OCH_3) 6.9–7.6 (m, 34 H, C_6H_5, C_6H_4)	18.20 (dd, J = 8.3, 6.4 Hz) 31.61 (dd, J = 32.1, 6.4 Hz) 36.99 (dd, J = 32.1, 8.3 Hz)
$(PPh_3)_2Ni(CH_3C(O)P(O)(OMe)_2)$ (4)		1259 1236	1.54 (m, 3 H, $C(O)CH_3$) 3.18 (d, J = 10.8 Hz, 3 H, OCH_3) 3.67 (d, J = 9.6 Hz, 3 H, OCH_3) 6.9–7.7 (m, 30 H, C_6H_5)	18.38 (d, J = 12.2 Hz) 28.46 (d, J = 34.2 Hz) 37.97 (dd, J = 12.2, 34.2 Hz)
$(PPh_3)_2Ni(C_2H_5C(O)P(O)(OMe)_2)$ (5)		1261 1229	1.45 (m, 3 H, CH_2CH_3) 1.98 (m, 2 H, CH_2CH_3) 3.12 (d, J = 10.2 Hz, 3 H, OCH_3) 3.63 (d, J = 9.6 Hz, 3 H, OCH_3) 6.9–7.7 (m, 30 H, C_6H_5)	18.20 (d, J = 12.2 Hz) 27.73 (d, J = 34.2 Hz) 38.18 (dd, J = 12.2, 34.2 Hz)

^{a} In C_6H_6. ^{b} In C_6D_6. ^{c} In THF.

bond axis occurs freely, the π-coordination of the α-keto phosphonate to the Ni makes the carbonyl carbon an optical active center, then the two OMe groups become diastereotopic. From the ^{31}P{^{1}H} NMR data described later, no propeller-like movement has been demonstrated in the NMR time scale. Although it is unclear at present whether the P–C bond rotates freely or not, it can be said that the coordinating α-keto phosphonate does not dissociate and does not rotate about the C=O axis in the coordination sphere faster than the NMR time scale.

The ^{31}P{^{1}H} NMR spectra exhibit three doublets of doublet for the aryl keto phosphonate complexes and one doublet of doublet and two doublets for the alkyl keto phosphonate complexes. To assign these resonances, the selective decoupling measurements were carried out for complex 1 (Figure 1). The nondecoupled ^{31}P NMR spectrum (B) exhibits three broad resonances. The two resonances at 31.31 and 37.03 ppm change to a doublet of doublets on proton irradiation with the resonance frequency for the phenyl protons, and the resonance at 18.59 ppm remains broad (C). When the resonance frequency for the methoxy protons is irradiated, the resonance at 18.59 ppm becomes a doublet of doublets and two resonances at 31.31 and 37.03 ppm are still broad (D). Thus, the resonance at 18.59 ppm can be ascribed to P in the α-keto phosphonate, which is coupled with two triphenylphosphines with 7.4- and 4.9-Hz coupling constants, and both resonances at 31.31 and 37.03 ppm can be assigned to P in the triphenylphosphines, which are coupled with each other at 34.1 Hz. For a square-planar complex, the coupling constant between two nuclei trans to each other is greater than that between two nuclei cis to each other. Thus, the resonance at 37.03 ppm with a greater coupling constant (J_{PP} = 7.4 Hz) is presumably due to the triphenylphosphine trans to the coordinating carbonyl carbon in the phenyl keto phosphonate. The ^{31}P{^{1}H} NMR resonances can be similarly assigned for 2–5. The geometrical rigidity around the Ni atom in the NMR time scale is deduced from the distinct ^{31}P{^{1}H} NMR spectra.

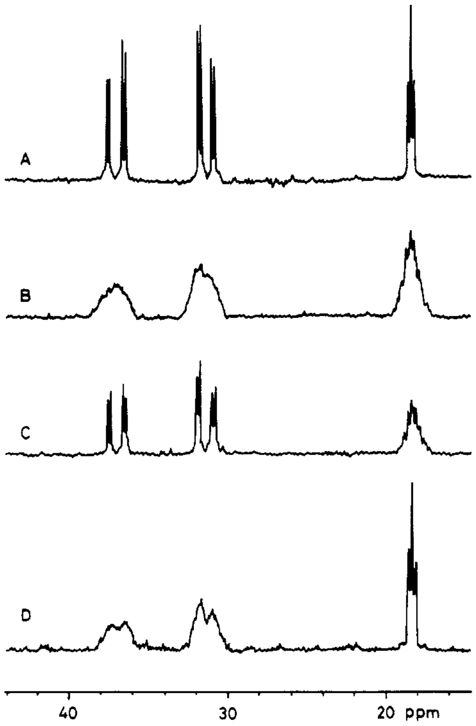

Figure 1. ^{31}P NMR spectra of 1: (A) all protons irradiated; (B) no protons irradiated; (C) phenyl protons irradiated selectively; (D) methoxy protons irradiated selectively.

Crystal Structure of $(PPh_3)_2Ni(\eta^2$-$(CO)EtC(O)P(O)(OMe)_2)$. We sought to verify the structure of an α-keto phosphonate complex by X-ray crystallography.

Table II. Summary of Crystal Data, Intensity Collection, and Structure Solution and Refinement for $(PPh_3)_2Ni(\eta^2\text{-}(CO)EtC(O)P(O)(OMe)_2)$ (5)

formula	$C_{41}H_{41}NiO_4P_3$
crystal system	monoclinic
space group	$P2_1/n$
cell constants	
a, Å	9.640 (3)
b, Å	18.910 (8)
c, Å	20.821 (8)
β, deg	90.03 (3)
V, Å^3	3796 (2)
Z	4
D_{calcd}, g cm^{-3}	1.311
D_{obsd}, g cm^{-3}	1.300
μ_{calcd}, cm^{-1}	6.748
crystal size, mm	0.23 × 0.35 × 0.33
radiation	Mo Kα (λ 0.71069 Å), graphite monochromator
scan technique	ω
scan range, deg	$3 < 2\theta < 40$
unique data	3959
unique data, $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	2854
R_1	0.049
R_2	0.051

Table III. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

Bond Distances			
Ni–P1	2.217 (2)	P2–C231	1.839 (7)
Ni–P2	2.136 (2)	C1–O1	1.336 (8)
Ni–C1	1.949 (7)	C1–C2	1.505 (10)
Ni–O1	1.851 (5)	C2–C3	1.503 (12)
Ni–O2	3.187 (5)	C1–P3	1.810 (7)
P1–C111	1.826 (7)	P3–O2	1.450 (6)
P1–C121	1.826 (8)	P3–O3	1.581 (6)
P1–C131	1.830 (8)	P3–O4	1.569 (6)
P2–C211	1.811 (7)	O3–C4	1.394 (13)
P2–C221	1.837 (7)	O4–C5	1.419 (11)
Bond Angles			
P1–Ni–P2	106.12 (8)	C1–P3–O2	116.27 (33)
P1–Ni–O1	98.61 (16)	C1–P3–O3	106.99 (32)
P2–Ni–C1	114.17 (21)	C1–P3–O4	103.23 (33)
C1–Ni–O1	41.07 (25)	O2–P3–O3	112.33 (32)
Ni–P1–C111	112.09 (24)	O2–P3–O4	116.01 (33)
Ni–P1–C121	122.55 (25)	O3–P3–O4	100.49 (32)
Ni–P1–C131	110.15 (25)	Ni–O1–C1	73.43 (36)
C111–P1–C121	104.06 (33)	P3–O3–C4	120.35 (63)
C111–P1–C131	103.14 (33)	P3–O4–C5	122.86 (54)
C121–P1–C131	102.86 (34)	Ni–C1–O1	65.51 (34)
Ni–P2–C211	110.73 (23)	Ni–C1–C2	123.05 (50)
Ni–P2–C221	120.32 (24)	O1–C1–C2	119.26 (59)
Ni–P2–C231	115.08 (24)	Ni–C1–P3	109.50 (30)
C211–P2–C221	102.30 (32)	O1–C1–P3	112.14 (47)
C211–P2–C231	107.07 (32)	C2–C1–P3	117.05 (50)
C221–P2–C231	99.77 (33)	C1–C2–C3	114.21 (65)

Table IV. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms

atom	x	y	z	B_{eq}, Å^2
Ni	4900 (1)	3024 (0)	4042 (0)	2.8
P1	4860 (2)	1992 (1)	4548 (1)	3.2
P2	2818 (2)	3410 (1)	4056 (1)	3.0
P3	5844 (2)	3604 (1)	2737 (1)	4.0
O1	6750 (4)	3030 (2)	3804 (2)	3.8
O2	5028 (5)	3009 (3)	2513 (2)	5.0
O3	7287 (6)	3660 (3)	2379 (3)	5.7
O4	5231 (6)	4357 (3)	2594 (2)	5.9
C1	6202 (7)	3634 (4)	3589 (3)	3.4
C2	6715 (8)	4325 (4)	3859 (4)	4.3
C3	6776 (9)	4348 (4)	4579 (4)	5.3
C4	8092 (10)	3058 (6)	2280 (5)	8.4
C5	4583 (9)	4533 (5)	2003 (4)	5.6
C111	5914 (7)	2002 (4)	5277 (3)	3.7
C112	5739 (9)	1579 (5)	5806 (4)	6.2
C113	6596 (10)	1625 (6)	6329 (4)	7.9
C114	7675 (9)	2091 (6)	6329 (4)	6.9
C115	7878 (9)	2526 (5)	5815 (4)	6.1
C116	7008 (8)	2467 (4)	5290 (4)	4.7
C121	3248 (7)	1565 (4)	4796 (3)	4.1
C122	2616 (8)	1047 (4)	4437 (4)	5.0
C123	1328 (10)	783 (5)	4602 (5)	6.8
C124	637 (9)	1031 (5)	5129 (5)	7.7
C125	1261 (9)	1537 (5)	5495 (4)	6.2
C126	2541 (8)	1811 (4)	5338 (4)	4.8
C131	5695 (7)	1312 (4)	4056 (3)	3.8
C132	5826 (8)	1435 (4)	3409 (4)	4.4
C133	6440 (9)	935 (5)	3021 (4)	6.0
C134	6897 (10)	313 (5)	3285 (5)	7.8
C135	6813 (11)	188 (5)	3925 (6)	8.2
C136	6190 (10)	690 (4)	4313 (4)	6.1
C211	1633 (7)	2755 (3)	3738 (3)	3.2
C212	2028 (8)	2428 (4)	3174 (4)	4.4
C213	1205 (9)	1934 (5)	2883 (4)	5.8
C214	−18 (9)	1727 (4)	3161 (5)	6.0
C215	−432 (8)	2033 (4)	3724 (4)	5.5
C216	386 (8)	2539 (4)	4015 (4)	4.6
C221	2346 (7)	4204 (4)	3598 (3)	3.4
C222	1353 (8)	4211 (4)	3124 (4)	4.7
C223	1053 (10)	4825 (5)	2791 (4)	6.5
C224	1738 (9)	5443 (4)	2945 (4)	5.9
C225	2706 (9)	5450 (4)	3425 (4)	5.5
C226	3013 (8)	4828 (4)	3747 (3)	4.1
C231	2165 (7)	3664 (3)	4853 (3)	3.5
C232	860 (8)	3972 (4)	4927 (3)	4.1
C233	429 (9)	4162 (4)	5538 (4)	5.1
C234	1288 (9)	4058 (4)	6052 (4)	5.4
C235	2571 (9)	3772 (4)	5989 (4)	5.4
C236	3025 (8)	3576 (4)	5374 (3)	3.8

X-ray data were collected on a crystal of **5** as summarized in Table II. Refinement, described in the Experimental Section, yielded the structure shown in Figure 2. The selected bond distances and angles are listed in Table III. The final atomic coordinates for non-hydrogen and hydrogen atoms and the final thermal parameters are given in Tables IV, V, and VI, respectively (Tables V and VI are given in the supplementary material (see the paragraph at the end of the paper)). Observed and calculated structure factors are listed in Table VII (supplementary material).

The X-ray structure revealed that the ethyl keto phosphonate coordinates to the nickel atom through a C═O π-bond. The η^2-(CO) coordination mode of an organic carbonyl group to a group 10 transition metal determined by X-ray analysis has been limited to two examples to our knowledge: $(PPh_3)_2Ni(\eta^2\text{-}(CO)(CF_3)_2CO)$ (A)[12] and $(PEt_3)_2Ni(\eta^2\text{-}(CO)Ph_2CO)$[7e] (B). Let us examine the structure of **5** in comparison with the other two examples. The geometry around Ni is planar (the sum of angles around the Ni is 359.97°) and in the other two cases as well. The bond distances are different between the two Ni–P. The Ni–P1 bond trans to C1 is longer than the Ni–P2 bond trans to O1 by 0.081 Å. This tendency has been observed for both A and B, and thus it can be said that the carbon atom has stronger trans influence than the oxygen atom in a π-coordinating ketone for square-planar transition-metal complexes. The C1–O1 bond distance is 1.336 Å, which is very close to the C═O lengths for A (1.32 Å) and B (1.335 Å), being longer than those for the corresponding free ketones. Although it is unable to compare the C═O bond lengths between coordinating and uncoordinating α-keto phosphonates because of the lack of X-ray data for free α-keto phosphonates, it is reasonable to expect that the C═O bond of ethyl keto phosphonate also lengthens on coordination to Ni.

The four atoms of O1, C1, C2, and P3 do not form an ideal plane (the sum of angles around C1 is 348.45°). The

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[12] Countryman, R.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1972**, *2*, 281.

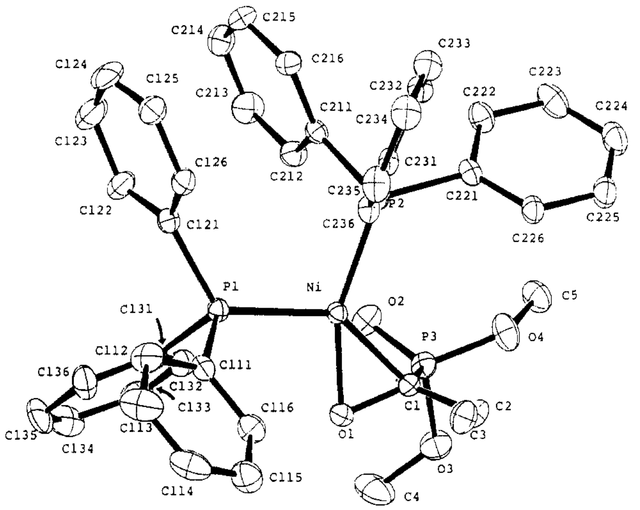
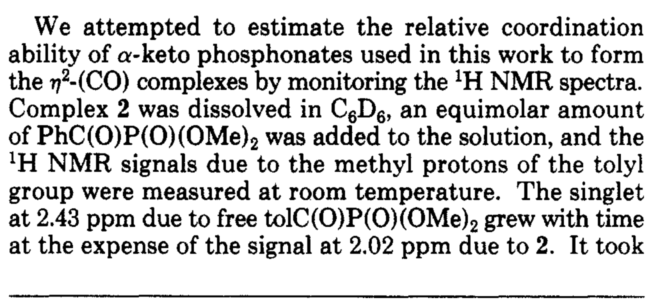


Figure 2. ORTEP drawing of 5 showing a labeling scheme. Thermal ellipsoids are drawn at 20% probability level.

two δ angles,[7a] i.e., in this case, the two dihedral angles between the Ni–C1–O1 plane and C1–O1–P3 plane and between the Ni–C1–O1 plane and C1–O1–C2 plane are 102.16° and 115.55°, respectively. The bending back of the substituents on the carbonyl carbon against the Ni may be due to the significant back-donation from the filled d-orbital of Ni to the empty π^*-orbital of the C=O bond.

The phosphoryl oxygen (O2) is situated above the Ni atom and seems to occupy the apical position of the tetragonal pyramidal structure of the Ni atom. The distance between Ni and O2 is 3.187 Å, which is very close to the sum of the van der Waals radii of Ni and O (3.10 Å). The phosphoryl bond length observed for 5 (1.450 Å) is close to that for other free phosphonate compounds.[13] It seems to be unreasonable that the phosphoryl oxygen is located above the Ni by chance in the crystal due to the packing restriction. Thus, we can expect that there is some interaction between Ni and O2, but it may be very weak.

Coordination Ability of α-Keto Phosphonates. The complexes 1–5 are stable in C_6H_6 and THF, and free α-keto phosphonate was not detected when they were dissolved in these solvents. However, on addition of another kind of α-keto phosphonate, an exchange reaction was observed, as expressed in eq 7.



(7)

We attempted to estimate the relative coordination ability of α-keto phosphonates used in this work to form the η^2-(CO) complexes by monitoring the ^1H NMR spectra. Complex 2 was dissolved in C_6D_6, an equimolar amount of $PhC(O)P(O)(OMe)_2$ was added to the solution, and the ^1H NMR signals due to the methyl protons of the tolyl group were measured at room temperature. The singlet at 2.43 ppm due to free $tolC(O)P(O)(OMe)_2$ grew with time at the expense of the signal at 2.02 ppm due to 2. It took about 2 h to attain the equilibrium. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution as well showed the formation of free $tolC(O)P(O)(OMe)_2$ and 1. Although we could not obtain the correct equilibrium constant and the exchange rate because of the appearance of some unidentified signals in the ^1H and $^{31}P\{^1H\}$ NMR spectra, the relative coordination ability of α-keto phosphonates toward the $Ni(PPh_3)_2$ moiety was obtained in this way. The order is as follows:

$$p\text{-}ClC_6H_4C(O)P(O)(OMe)_2 > C_6H_5C(O)P(O)(OMe)_2 > p\text{-}MeC_6H_4C(O)P(O)(OMe)_2 > MeC(O)P(O)(OMe)_2 = EtC(O)P(O)(OMe)_2$$

The stability of the nickel–α-keto phosphonate bond is enhanced by electron-withdrawing substituents and is reduced by electron-donating groups. This tendency is consistent with the generalized Dewar–Chatt–Duncanson model for olefin bonding that electron back-donation from a filled metal d-orbital to an empty olefin π^*-orbital is predominant. The similar ^1H NMR measurements revealed the following relative π-coordination ability toward $(PPh_3)_2Ni$ moiety:

$$CH_2{=}CHCN > RC(O)P(O)(OMe)_2 > PhC(O)Ph$$

Table VIII. Values of ν_{NC} in $Ni(t\text{-}BuNC)_2(R^1C(O)R^2)$ (cm^{-1})

R^1	R^2	ν_{NC}	
Ph	CO_2Et	2163	2124[a]
Ph	CO_2Me	2164	2128[a]
Ph	$P(O)(OMe)_2$	2167	2131[b]
Ph	CF_3	2169	2130[a]
Ph	CN	2173	2138[a]
Me	CO_2Me	2158	2118[a]
Me	$P(O)(OMe)_2$	2163	2123[b]
Me	CF_3	2165	2120[a]

[a] Reference 7c. [b] This work.

Ittel reported the isocyanide stretching frequencies for many $Ni(t\text{-}BuNC)_2$(unsaturated molecule) complexes involving ketones and established the relationship of the π-acceptor properties of the unsaturated bond with the electronegativity of the substituent groups.[7c] An α-keto phosphonate may be taken as a ketone having a phosphonate substituent ($-P(O)(OR)_2$). Thus, we attempted to establish the electronegativity of a phosphonate group by measuring the ν_{NC} of $Ni(t\text{-}BuNC)_2(\eta^2\text{-}(CO)\text{-}\alpha\text{-keto phosphonates})$. The results are listed in Table VIII together with the values reported by Ittel. For the cases of both phenyl keto phosphonate and methyl keto phosphonate, these frequencies are close to those for $PhC(O)CF_3$ and $MeC(O)CF_3$, respectively, indicating that a $P(O)(OMe)_2$ group is as electronegative as a CF_3 group.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. All solvents used, benzene, toluene, Et_2O, THF, and hexane, were purified by distillation from sodium metal and stored under a nitrogen atmosphere. α-Keto phosphonates were prepared from the corresponding acid chlorides and trimethyl phosphite by the Arbuzov reaction according to the literature methods.[14] $Ni(cod)_2$ was prepared from $Ni(acac)_2$, $AlEt_3$, and 1,5-cyclooctadiene (cod) in toluene according to the literature method.[15]

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IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. JEOL PMX-60 and FX-100 spectrometers were used to obtain ^{1}H and ^{31}P{^{1}H} NMR spectra, respectively. ^{1}H NMR data were referenced to $(CH_3)_4Si$, and ^{31}P{^{1}H} NMR data were referenced to 85% H_3PO_4.

Preparation of $(PPh_3)_2Ni(\eta^2\text{-}(CO)PhC(O)P(O)(OMe)_2)$ (1). $PhC(O)P(O)(OMe)_2$ (330 mg, 1.539 mmol) was added to a solution of $Ni(cod)_2$ (141 mg, 0.513 mmol) and PPh_3 (170 mg, 1.03 mmol) in 2 mL of Et_2O. A yellowish orange precipitate was formed after several minutes. The heterogeneous solution was stirred for 3 h. The precipitate was isolated by filtration, washed with hexane for several times, and dried in vacuo to give 1 (300 mg, 0.376 mmol, 73%). Anal. Calcd for $C_{45}H_4NiO_4P_3$: C, 67.78; H, 5.18. Found: C, 68.08; H, 4.88.

Preparation of $(PPh_3)_2Ni(\eta^2\text{-}(CO)\text{-}p\text{-}MeC_6H_4C(O)P(O)(OMe)_2)$ (2). $p\text{-}MeC_6H_4C(O)P(O)(OMe)_2$ (600 mg, 2.63 mmol) was added to a solution of $Ni(cod)_2$ (270 mg, 0.98 mmol) and PPh_3 (530 mg, 2.02 mmol) in 2 mL of Et_2O. A yellowish orange precipitate formed by 3 h stirring at room temperature was isolated by filtration, washed with hexane, and dried in vacuo to give **2** (575 mg, 0.709 mmol, 72%). Anal. Calcd for $C_{46}H_{43}NiO_4P_3$: C, 68.09; H, 5.34. Found: C, 67.76; H, 5.58.

Preparation of $(PPh_3)_2Ni(\eta^2\text{-}(CO)\text{-}p\text{-}ClC_6H_4C(O)P(O)(OMe)_2)$ (3). $p\text{-}ClC_6H_4C(O)P(O)(OMe)_2$ (303 mg, 1.22 mmol) was added to a solution of $Ni(cod)_2$ (114 mg, 0.414 mmol) and PPh_3 (240 mg, 0.915 mmol) in 2 mL of Et_2O. A yellowish orange precipitate formed by 2 days of stirring at room temperature was isolated by filtration, washed with hexane, and dried in vacuo to give 3 (224 mg, 0.269 mmol, 65%). Anal. Calcd for $C_{45}H_{40}ClNiO_4P_3$: C, 64.97; H, 4.85. Found: C, 64.81; H, 4.89.

Preparation of $(PPh_3)_2Ni(\eta^2\text{-}(CO)MeC(O)P(O)(OMe)_2)$ (4). $MeC(O)P(O)(OMe)_2$ (286 mg, 1.88 mmol) was added to a solution of $Ni(cod)_2$ (173 mg, 0.629 mmol) and PPh_3 (350 mg, 1.33 mmol) in 2 mL of Et_2O. A yellow precipitate was formed immediately. The heterogeneous solution was stirred for 30 min at room temperature. The yellow precipitate was isolated by filtration, washed with hexane, and dried in vacuo to give 4 (365 mg, 0.496 mmol, 79%). Anal. Calcd for $C_{40}H_{39}NiO_4P_3$: C, 65.33; H, 5.35. Found: C, 65.19; H, 5.16.

Preparation of $(PPh_3)_2Ni(\eta^2\text{-}(CO)EtC(O)P(O)(OMe)_2)$ (5). $EtC(O)P(O)(OMe)_2$ (385 mg, 2.26 mmol) was added to a solution of $Ni(cod)_2$ (207 mg, 0.753 mmol) and PPh_3 (420 mg, 1.60 mmol) in 2 mL of Et_2O. A yellow precipitate was formed after 10 min. The heterogeneous solution was stirred for 2 h at room temperature. The yellow precipitate was isolated by filtration, washed with hexane, and dried in vacuo to give **5** (500 mg, 0.667 mmol, 89%). Anal. Calcd for $C_{41}H_{41}NiO_4P_3$: C, 65.71; H, 5.51. Found: C, 65.21; H, 5.60.

X-ray Data Collection, Structure Determination, and Refinement of 5. The single crystal of **5** obtained from the THF solution was sealed under N_2 in a thin-walled glass capillary. The determination of cell constants and the intensity data collection were carried out at room temperature on a Syntex R3 diffractometer with Mo Kα radiation made monochromatic by a graphite plate ($\lambda = 0.7107$ Å). The crystal system is not orthorhombic but monoclinic because β has a significant deviation from a right angle, which was confirmed by taking axial photographs: the b axial photograph exhibits a mirror symmetry while the a axial and c axial photographs do not exhibit this symmetry. The space group was uniquely determined as $P2_1/n$ from the systematic absences. Unit cell constants were determined by least-squares refinement of 25 reflections. Three reference reflections monitored after every cycle of 200 measurements showed no significant variation in intensity during the data collection. Out of 3959 unique reflections measured, 2854 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. The data were corrected for Lorentz-polarization factors, but no absorption correction was applied (μ(Mo Kα) = 6.748 cm^{-1}).

The positions of the Ni atoms were determined by direct methods (MULTAN 78).[16] All other computations were carried out by use of the universal difference Fourier computation program system, UNICS III.[17] Subsequent difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. After all the non-hydrogen atoms had been refined isotropically, a series of refinements were carried out by using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed at idealized positions. In the final stage, non-hydrogen atoms were refined anisotropically, including hydrogen atoms whose positions were fixed ($B = 4$ Å^2). At final refinement R_1 converged to 0.049 and R_2 to 0.051. All the atomic scattering factors were taken from Cromer and Waber.[18] The anomalous dispersion coefficients of Cromer and Liberman[19] were used for Ni and P. All the computations including the ORTEP drawings[20] were carried out on a HITAC R-640 computer at the Hiroshima University Information Processing Center.

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Supplementary Material Available: Tables of calculated hydrogen atom parameters and anisotropic thermal parameters for **5** (Tables V and VI) (4 pages); a listing of observed and calculated structure factors (Table VII) (13 pages). Ordering information is given on any current masthead page.

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