Registry No. $[Co(As_2S)(triphos)]BF_4$, 88887-22-3; $[Co\{SAsC(Ph)_2As\}(triphos)]BF_4$, 97074-05-0; $CuI[P(OMe)_3]$, 34836-53-8; diphenyldiazomethane, 883-40-9.

Supplementary Material Available: Listings of positional and thermal parameters, all bond distances and angles, and structure factors (24 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of $(C_5Me_5)(CO)_2RuP[C(O)(t\text{-Bu})]_2$, the First Diacylphosphido Complex with Metal–Phosphorus Coordination

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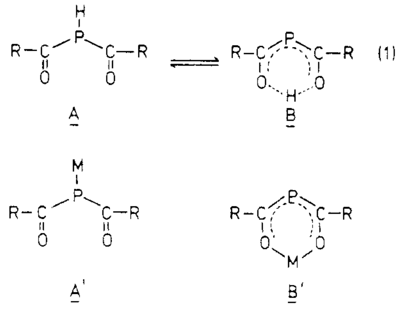
Summary: The disilylphosphido complex $(C_5Me_5)(CO)_2RuP(SiMe_3)_2$ reacts with 2 equiv of pivaloyl chloride to produce the novel dipivaloylphosphido complex $(C_5Me_5)(CO)_2RuP[C(O)(t\text{-Bu})]_2$ in which metal phosphorus coordination is encountered instead of the usual chelation via the oxygen atoms. An X-ray structural determination reveals the presence of a pair of enantiomeric molecules of the complex in the asymmetric unit. The two pivaloyl substituents at the trigonal-pyramidal phosphorus atom are accommodated as right- and left-oriented propellers. The ruthenium–phosphorus distance of 2.404 (1) Å is in accord with a single bond between these atoms.

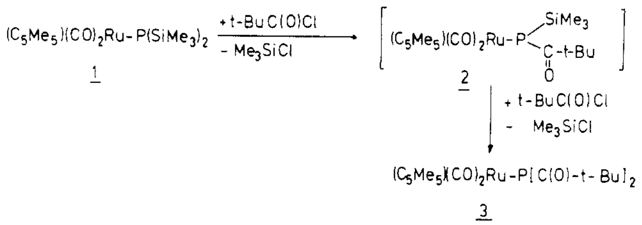
The chemistry of compounds with carbon–phosphorus multiple bonds is an area of current interest to both theoretical and preparative chemists.[2] It is known that in solution diacylphosphines exist in a keto–enol equilibrium according to eq 1,[3] whereas in the crystalline state the enol



structure B clearly is present (for R = *t*-Bu).[4] A similar situation has been encountered in *β*-diketones, the anions of which are valuable and versatile ligands. Analogously diacylphosphides should readily coordinate to metal, yielding complexes of type A′ and/or B′.

In lithium,[5] aluminum,[6] chromium, and nickel[2b,3] derivatives the diacylphosphides serve as chelating ligands via the oxygen atoms (B′). A simple method for the preparation of a ruthenium diacylphosphido complex, **3**, with the hitherto unknown coordination mode A′, is reported here along with the X-ray structure analysis of this complex.

Scheme I



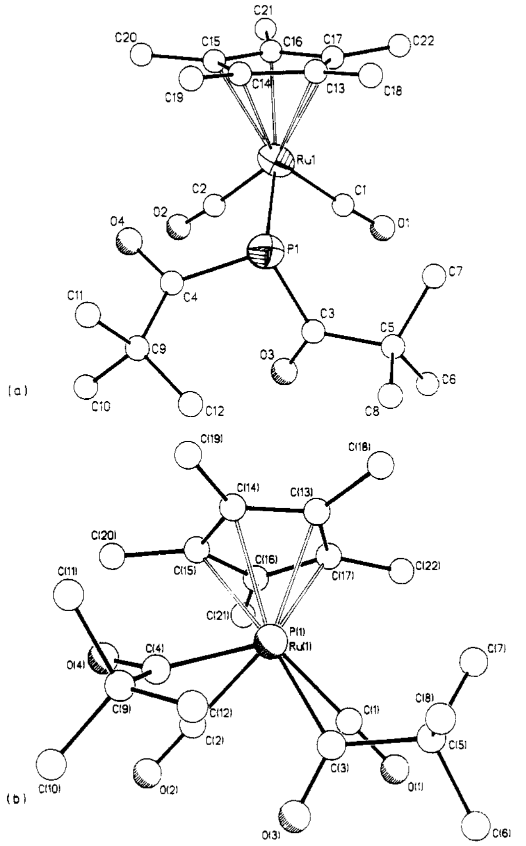


Figure 1. Two views of the molecular structure of $(\eta^5\text{-}C_5Me_5)(CO)_2RuP[C(O)(t\text{-Bu})]_2$ (**3**). (b) approximates a Newman projection down the P(1)Ru(1) bond.

Table I. Selected Bond Lengths (Å) and Angles (deg) with Errors for $(C_5Me_2)(CO)_2RuP[C(O)(t\text{-Bu})]_2$ (Given for Molecule I)

atoms	bond length	atoms	angle
Ru-P1	2.404 (1)	P1-Ru-C1	96.0 (1)
Ru-C1	1.867 (3)	P1-Ru-C2	92.0 (1)
Ru-C2	1.889 (4)	C1-Ru-C2	88.4 (2)
$Ru-C_{ring}$ (av)	2.246	Ru-P1-C3	105.9 (1)
P1-C3	1.873 (3)	Ru-P1-C4	105.0 (1)
P1-C4	1.873 (4)	C3-P1-C4	101.9 (2)
C1-O1	1.139 (4)	P1-C4-C9	123.6 (3)
C2-O2	1.130 (5)	P1-C4-O4	118.6 (3)
C3-O3	1.205 (4)	O4-C4-C9	116.1 (3)
C4-O4	1.204 (5)	P1-C3-C5	118.3 (2)
C3-C5	1.554 (5)	P1-C3-O3	121.5 (3)
C4-C9	1.536 (4)	O3-C3-C5	120.1 (3)
		Ru-P1-C4-O4	−19.9
		C3-P1-C4-O4	130.2
		Ru-P1-C3-O3	−86.9
		C4-P1-C3-O3	22.7
		C1-Ru-P1-C3	−14.2
		C2-Ru-P1-C4	−33.0

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The reaction of $(C_5Me_5)(CO)_2RuP(SiMe_3)_2$ (1)[7] with 2 equiv of pivaloyl chloride in cyclopentane (20 °C, 1 h) yields a yellow solution. Evaporation to dryness and crystallization of the residue from pentane produces a 77% yield of a yellow microcrystalline solid. Recrystallization from pentane at -30 °C yields large orange-yellow crystals suitable for X-ray diffraction (Scheme I).

The structure of **3** was assigned on the basis of spectral evidence and confirmed by a single-crystal X-ray diffraction study.[8] The asymmetric unit of the structure of complex **3** comprises a pair of enantiomeric molecules. One enantiomer is shown in Figure 1, and selected bond distances and angles are presented in Table I. The coordination of the dipivaloylphosphido ligand in **3** is of primary interest. The trigonal-pyramidal phosphorus atom is ligated by the $(C_5Me_5)(CO)_2Ru$ unit and two propeller-like oriented pivaloyl groups. The oxygen atoms of the carbonyl dipoles are directed away from the phosphorus atom, thus minimizing interactions between the π-electrons and the free electron pair on phosphorus.

The phosphorus ligand adopts a conformation in which the lone pair is orthogonal to the ruthenium HOMO. The torsion angle between the $P[C(O)(t\text{-Bu})]_2$ lone pair and the ruthenium fragment HOMO (taken as Ru–C101 bond) is 112°. The position of the lone pair was assumed in the plane bisecting the C3–P–C4 angle. The torsion angle D1–P1–Ru1–C1 (D1 symbolizes the middle of the ring ligand) is 100.7°. Stereochemical activity of the phosphorus lone pair in transition-metal phosphido complexes, which has been recently pointed out by Gladysz as "gauche effect in transition-metal chemistry",[9] is also evident in the crystal structures of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2PPh_2$,[10] $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\overline{PN(Me)CH_2CH_2NMe})$,[11] and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)PPh_2$.[9] The ruthenium to phosphorus bond (2.404 (1) Å) is only slightly shorter than the calculated value for a Ru–P single bond (2.43 Å).[12,13] The phosphorus carbon (CO) distances are close to the calculated single bond values (1.85 Å),[14] whereas the CO distances of the acylic carbonyl functions are essentially those of localized CO double bonds.

The simplicity of the ^1H NMR (C_6D_6, 200 MHz; δ 1.40 (s, 18 H, *t*-Bu), 1.54 (d, J = 1.2 Hz, 15 H, C_5Me_5)) and ^{13}C NMR spectra (C_6D_6, 50.309 MHz; δ_C 9.54 (d, $^3J_{PC}$ = 4.6 Hz, $C_5(CH_3)_5$), 27.92 (d, $^3J_{PC}$ = 3.7 Hz, $C(CH_3)$), 49.06 (d, $^2J_{PC}$ = 29.1 Hz, $C(CH_3)$), 100.29 (s, $C_5(CH_3)_5$), 202.50 (s, RuCO), 235.66 (d, $^1J_{PC}$ = 71.0 Hz, PC(O)) suggests that in solution both pivaloyl groups rotate freely around the P–C bonds and that this rotation is rapid on the ^1H and ^{13}C NMR time scale at room temperature. At -100 °C (in toluene-d_8) each *tert*-butyl group gives rise to a singlet in the ^1H NMR spectrum (δ_H 0.86 and 0.95). The phosphorus signal is a singlet at δ_P 56.7 (85% H_3PO_4 standard) at room temperature (in C_6D_6). At -100 °C (toluene-d_8) this signal is slightly broadened and is seen at 52.58 ppm. From the position of the ^{13}CO signals of the carbonyl ligands in **3** and **1** (δ_C 204.5) it is clear that the divaloylphosphido group is a much better acceptor ligand than the $P(SiMe_3)_2$ ligand in **1**.[15] This evidence is supported by two strong infrared absorptions of the $Ru(CO)_2$ moiety in **3** at 2038 and 1967 cm^{-1} (in hexane) (**1**: ν(CO) = 2012, 1953 cm^{-1} in hexane). In Nujol two strong bands at 1632 and 1610 cm^{-1}, which in CH_2Cl_2 solution collapse to a broad band at 1620 cm^{-1}, are attributed to the CO stretching modes of the pivaloyl groups.

A probable mechanism for the formation of **3** is depicted in Scheme I. Reaction of **1** with pivaloyl chloride is presumed to give the intermediate complex **2**, which is rapidly consumed by a second mole of pivaloyl chloride, thus preventing the isolation or spectroscopic characterization of **2**. The attempted preparation of **2** by reacting equimolar amounts of **1** and *t*-BuC(O)Cl yields a 1:1 mixture of **3** and unreacted **1**. Although not observed in this case rearrangement products of species such as **2** (cf. $(C_5H_5)(CO)_2FeP{=}C(OSiMe_3)(t\text{-Bu})$[16]) may be obtained from the reaction of $(C_5H_5)(CO)_2FeP(SiMe_3)_2$ with pivaloyl chloride. Other reactions of $(R_5C_5)(CO)_2MP(SiMe_3)_2$ with acid chlorides are under investigation.

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Registry No. 1, 97889-65-1; 3, 97877-48-0; *t*-BuC(O)Cl, 3282-30-2.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic and isotropic thermal parameters, bond lengths, and bond angles (43 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for complex **3**: space group $P\bar{1}$, a = 9.954 (1) Å, b = 13.563 (3) Å, c = 18.072 (4) Å, α = 91.59 (2)°, β = 93.54 (2)°, γ = 96.84 (2)°, V = 2416 (1) $Å^3$, Z = 4, ρ_{calcd} = 1.36 g/cm^3; μ(Mo Kα, graphite-monochromator) = 7.2 cm^{-1}; $2\theta/\omega$ scan data collection at roomtemperature ($3° \leq 2\theta \leq 55°$); 6377 unique reflections, 5615 unique observed ($F_o \geq 3.50(F)$); Syntex R3-four circle diffractometer; structure solving by Patterson and difference Fourier techniques and refinement by block-cascade least squares, using SHELXTL on a NOVA 3 (Data General). All non-hydrogen atoms refined anisotropical with 554 parameters and rigid groups for cyclopentadienylrings and all hydrogen atoms, given the 1.2-fold isotropic temperature factor of the $\mathbf{U}_{ij}$ tensor of the corresponding C atom; R = 0.030, R_w = 0.034, $w^{-1} = \sigma^2(F) + 0.0004F^2$, maximum rest electron density 0.38 e/$Å^3$.

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Isomerization of a Symmetrical Metal–Metal Bonded Gold(II) Ylide Dimer to a Mixed-Valence Gold(III)/Gold(I) Species

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Summary: The first example of the spontaneous isomerization of a metal–metal bonded gold(II) ylide dimer to its mixed-valence Au(III)/Au(I) isomer is reported. This isomerization occurs in nitromethane and other weakly protonic solvents, such as acetone. The X-ray structure of the mixed-valence species shows the presence of a 3.184 (1) Å Au(III)/Au(I) distance.

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