ORGANOMETALLICS

Generation and stabilization of the 3,3-diphenyl-1,2,4-thiadiarsete unit at a transition metal

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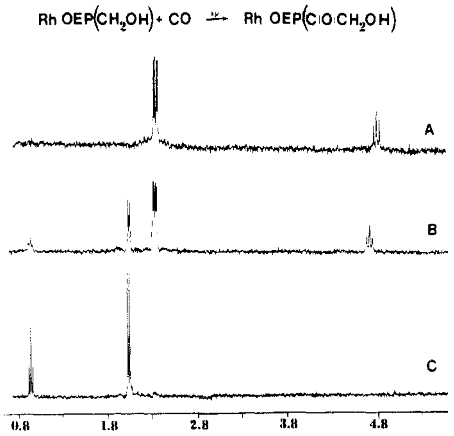

Figure 2. (A) High-field region of the ^1H NMR of RhOEP(CH_2OH) pressurized with CO (P_{CO} = 320 torr) in C_6D_6 (time = 0). (B) ^1H NMR of solution A irradiated ($h\nu > 445$) for 30 min. (C) ^1H NMR of pure RhOEP[C(O)CH_2OH].

compound I and the corresponding alkyl complex RhOEP(CH_3) photolytically incorporate carbon monoxide to form the corresponding acyl derivatives (reactions 6 and 7). In a typical experiment the alkyl complex was irradiated, using a band path filter ($h\nu > 445$), for 90 min in the presence of 300 torr of carbon monoxide, at ice–water temperatures. The methylacyl complex III was characterized by comparison with authentic samples prepared by published procedures.[6] The hydroxyacyl complex IV has been characterized by proton and carbon-13 NMR and IR as well as mass spectra analysis (Figure 2).[7] The overall conversion to the hydroxyacyl complex IV is limited by the simultaneous photoinduced transformation of the hydroxymethyl complex I into metal hydride and formaldehyde. Further conversion to the hydroxyacyl species is accomplished by thermally regenerating the hydroxymethyl compound, followed by continued photolysis. A comparison of NMR and IR spectra for III and IV is compatible with the presence of intramolecular hydrogen bonding between the hydroxy and carbonyl functionalities, which has also been noted for the only previously reported metallohydroxyacyl complex.[8]

$$\mathrm{ROEP(CH_3)} + \mathrm{CO} \xrightarrow{h\nu} \underset{\mathrm{III}}{\mathrm{RhOEP[C(O)CH_3]}} \qquad (6)$$

$$\mathrm{RhOEP(CH_2OH)} + \mathrm{CO} \xrightarrow{h\nu} \underset{\mathrm{IV}}{\mathrm{RhOEP[C(O)CH_2OH]}} \qquad (7)$$

The rhodium porphyrin system has demonstrated many of the most important steps postulated[1] in the catalytic reduction of CO to organic products. The key steps in this process usually include (a) the activation of molecular hydrogen, (b) the incorporation of carbon monoxide into the metal–hydride to form the metalloformyl, (c) the reduction of the metalloformyl to the hydroxymethyl complex, and either (d) reductive elimination of methanol or (e) incorporation of another molecule of carbon monoxide to form the corresponding hydroxyacyl (Scheme I). Reaction steps a, b, d, and e have been observed and characterized in the rhodium porphyrin system.[9,10] Further studies of the catalytic reduction of the metalloformyl to the hydroxymethyl complex (step c) as well as the intermolecular reductive elimination of the hydroxyacyl to glycoaldehyde (step f) are now in progress.

Scheme I

(a) $\mathrm{M{-}M + H_2 \rightleftharpoons 2M{-}H}$

(b) $\mathrm{M{-}H + CO \rightleftharpoons M{-}C(O)H}$

(c) $\mathrm{M{-}C(O)H + H_2 \rightarrow M{-}CH_2OH}$

(d) $\mathrm{M{-}CH_2OH + M{-}H \rightarrow M{-}M + CH_3OH}$

(e) $\mathrm{M{-}CH_2OH + CO \rightarrow M{-}C(O)CH_2OH}$

(f) $\mathrm{M{-}C(O)CH_2OH + M{-}H \rightarrow M{-}M + HC(O)CH_2OH}$

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Registry No. I, 83691-18-3; II, 97645-15-3; III, 83691-22-9; IV, 97645-16-4; RhOEP(H), 63372-77-0; $(RhOEP)_2$, 63439-10-1; RhOEP(CH_3), 36643-85-3; CH_2O, 50-00-0.

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(7) ^1H NMR of IV (C_6D_6): using ^{12}C carbon monoxide and ^{12}C formaldehyde, δ −2.01 [d (J_{CH_2OH} = 5.8 Hz)], −0.88 [*t* (J_{CH_2OH} = 5.8 Hz)]; using ^{13}C carbon monoxide with ^{13}C formaldehyde, δ −2.01 [d of d ($^1J_{^{13}CCH_2}$ = 2.9 Hz, J_{CH_2OH} = 5.8 Hz)]. ^{13}C NMR (proton decoupled): δ +202.3 [d ($^1J_{Rh^{13}C}$ = 34.2 Hz)]. IR (cm^{-1}, KBr): ν_{CO} 1697, ν_{OH} 3424 (br). MS: *m/e* 694 (M^+).

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Generation and Stabilization of the 3,3-Diphenyl-1,2,4-thiadiarsete Unit at a Transition Metal

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Summary: The reaction of [Co(As_2S)(triphos)]BF_4 [triphos = 1,1,1-tris[(diphenylphosphino)methyl]ethane], which contains the thiadiarsiranediyl ring η^3 bonded to the metal, with a tenfold excess of diphenyldiazomethane produces the dark red complex [Co{SAsC$(Ph)_2$As}(triphos)]BF_4. An X-ray structural determination has shown that the [Co{SAsC$(Ph)_2$As}(triphos)]$^+$ cation contains the four-membered 3,3-diphenyl-1,2,4-thiadiarsete unit 1,2,4-η^3 linked to the Co(triphos) moiety. Such unprecedented four-membered ring is obtained through insertion of the diphenylcarbene into the homoatomic bond of the thiadiarsiranediyl unit.

Mononuclear metal complexes containing the homocyclic E_3 (E = P,[1] As[2]) or the heterocyclic E_2X (E = P, X = S, Se;[3] E = As, X = S[4]) inorganic units η^3 bonded to a

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metal atom have been described. Such coordinated rings are endowed with reactivity. Indeed, it has been found that several of the above complexes react with suitable metal–ligand moieties affording either compounds in which the cyclic unit acts as a bridging ligand without notable changes in geometry[1a,5] or compounds in which one bond of the cyclic unit is cleaved.[6] With respect to the latter mode of reaction we have found that the thiadiphosphiranediyl and thiadiarsiranediyl units η^3 bonded to cobalt in the complexes [Co(E_2S)(triphos)]BF_4 [E = P, As; triphos = 1,1,1-tris[(diphenylphosphino)methyl]ethane] undergo insertion by the carbene-like Pt(PPh_3)$_2$ group into their heteroatomic E–S bond to form metallathiadiphosphete or -thiadiarsete rings η^3 bonded to the Co(triphos) moiety.[6]

In this communication we report on the insertion of diphenylcarbene into the As–As bond of the thiadiarsiranediyl ring in the compound [Co(As_2S)(triphos)]BF_4 which yields the complex [Co{SAsC(Ph)$_2$As}(triphos)]BF_4 containing the new 3,3-diphenyl-1,2,4-thiadiarsete unit. This inorganic ring is 1,2,4-η^3 bound to the cobalt atom through its S and the two As atoms.

The addition of a tenfold excess of diphenyldiazomethane to a methyl ethyl ketone solution of [Co(As_2S)(triphos)]BF_4 produces, after refluxing at ca. 80 °C in an inert atmosphere for 3 h, a color change from orange to dark red due to formation of [Co{SAsC(Ph)$_2$As}(triphos)]BF_4 according to, e.g., eq 1. Pure crystals of the compound which is air-sensitive both in the solid state and in solution are obtained by addition of n-heptane and slow evaporation of the resulting solution; yield 40% based on the cobalt complex. The reaction between the parent cobalt complex and diphenyldiazomethane, 1:10 ratio, in methyl ethyl ketone solution is also accomplished either by UV irradiation (30 min) at room temperature or by warming (60 min) at ca. 40 °C in presence of a catalytic amount of CuI[P(OMe)$_3$]$_3$;[7] the compound [Co{SAsC(Ph)$_2$As}(triphos)]BF_4 is obtained as described above, in lower yield (ca. 25%). Carbon, hydrogen, arsenic, cobalt, phosphorus, and sulfur elemental analyses and solution conductivity agree with the proposed formula.

$$[\mathrm{Co(As_2S)(triphos)]BF_4} \xrightarrow{\mathrm{(Ph)_2CN_2}} [\mathrm{Co\{SAsC(Ph)_2As\}(triphos)]BF_4} \quad (1)$$

An X-ray structure determination[8] of a single crystal of the compound has shown that it consists of [Co{SAsC(Ph)$_2$As}(triphos)]$^+$ cations and BF_4^- anions. The 3,3-diphenyl-1,2,4-thiadiarsete unit is η^3 bonded to the cobalt atom (Figure 1) through the sulfur and the two arsenic atoms; the metal atom is also coordinated by the three phosphorus atoms of the triphos ligand. The four-membered ring which contains three main-group "naked" and the diphenylcarbene C atom is not planar, the dihedral angle between the planes passing through As(1) and As(2) and respectiely through S or C (Figure 1) being 127.3°.

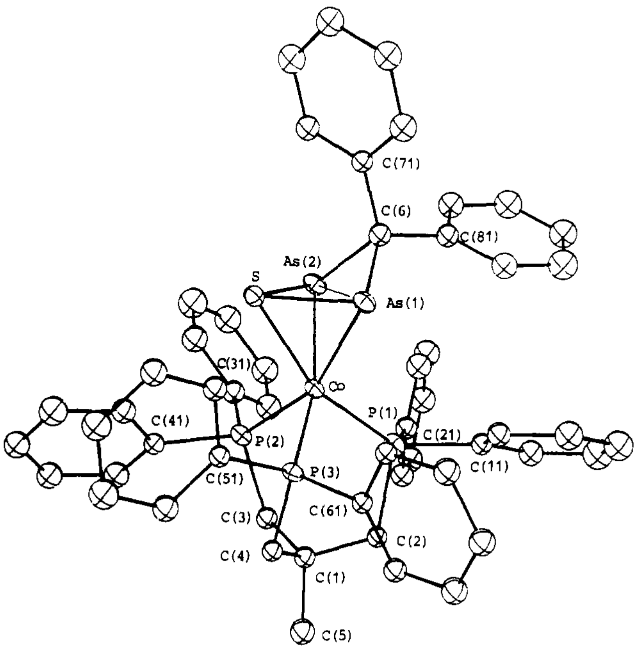

Figure 1. Perspective view of the [Co{SAsC(Ph)$_2$As}(triphos)]$^+$ cation. Only the first carbon atom of each phenyl group is labeled. Selected bond distances (Å) and angles (deg) are as follows: Co–P(1) = 2.189 (5), Co–P(2) = 2.262 (5), Co–P(3) = 2.268 (5), average S–As = 2.28, As(1)···As(2) = 2.850 (3), average C(6)–As = 2.01, average P–Co–P = 92.0, As(1)–Co–As(2) = 72.7 (1), average S–Co–As = 58.5, As(1)–S–As(2) = 77.2 (1), average S–As–C(6) = 83.7, As(1)–C(6)–As(2) = 90.4 (7).

Detailed structural comparisons with the parent [Co(As_2S)(triphos)]BF_4 compound are prevented by the orientational disorder of the As_2S ring in that compound.[4] The As–As bond elongates considerably upon insertion, from ca. 2.34 (1) Å (length of the longest side of the As_2S triangle in the parent cobalt complex, which is also the side with the highest As–As character[4] since it joins two sites with 0.85 As occupancy factors[4]) to 2.850 (3) Å. The shortening of the "Co–S" bond from 2.33 (1) Å to the present value of 2.263 (5) Å probably is only apparent, being rather due to loss of the partial Co–As character that this bond has in the parent compound. On the other hand, there are significant changes in the Co–P bond lengths: these span the 2.193 (4)–2.227 (4) Å range in the parent compound whereas in the present one the two Co–P bonds lying approximately trans to the Co–As ones are significantly longer [2.265 (4) Å, mean] than the third Co–P bond [2.189 (5) Å]. Such difference should be produced by the deformation undergone by the As_2S ring.

The alternative synthetic routes to [Co{SAsC(Ph)$_2$As}(triphos)]BF_4 described above were developed in order to obtain some insight into the process of insertion, considering in particular that diphenylcarbene is produced in the thermal or photolytic decomposition of diphenyldiazomethane,[9] as well as in presence of copper(I) compounds.[7] The viability of the different synthetic procedures and the need of a large excess of diphenyldiazomethane for the reactions to occur suggest that diphenylcarbene generated in situ inserts into the homoatomic bond of the As_2S ring, although this process is probably competing with additional reactions undergone by the radical.

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(8) X-ray diffraction data for $C_{41}H_{39}BAs_2CoF_4P_3S$: crystal size (mm) 0.10 × 0.30 × 0.30; monoclinic, space group $C2/c$; a = 25.393 (15) Å, b = 26.811 (16) Å, c = 16.932 (12) Å, β = 107.90 (9)°, V = 10969.5 Å^3, Z = 8 ρ(calcd) = 1.354 g cm^{-3}, M_w = 1118.56, μ(Mo Kα) = 16.74 cm^{-1}; poor crystalline material. Data were collected on a Phillips PW 1100 diffractometer: Mo Kα (graphite monochromated) radiation, λ = 0.71069 Å; 5108 measured reflections ($\pm h,k,l$; $5 < 2\theta < 44°$); 2683 unique observed ($I \geq 3\sigma(I)$) reflections; numerical correction for absorption applied (transmission coefficients 0.59–0.85). The structure was solved by a combination of heavy-atom and direct methods and refined by least-squares techniques (full matrix, 204 parameters) with anisotropic temperature factors assigned to the As, Co, P, and S atoms, rigid phenyl groups, and H atoms in calculated positions (C–H = 1.00 Å). The BF_4 anion is distributed over two positions, each with 0.50 occupancy: R = 0.068; R_w = 0.074 [$w = (\sigma^2_F + 0.0002F^2)^{-1}$].

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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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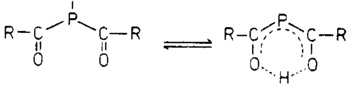
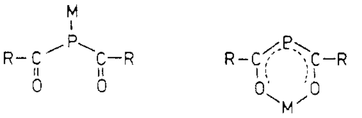
Summary: The disilylphosphido complex $(C_5Me_5)(CO)_2RuP(SiMe_3)_2$ reacts with 2 equiv of pivaloyl chloride to produce the novel dipivaloylphosphido complex $(C_5Me_5)(CO)_2RuP[C(O)(t\text{-}Bu)]_2$ in which metal phosphorus coordination is encountered instead of the usual chelation via the oxygen 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



(1)

A B

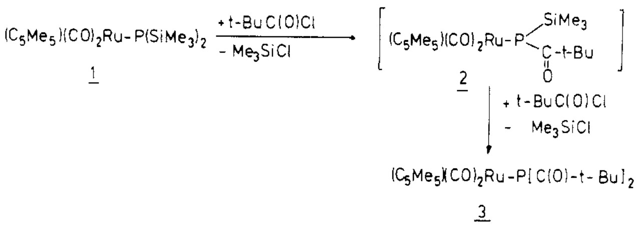


A' B'

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



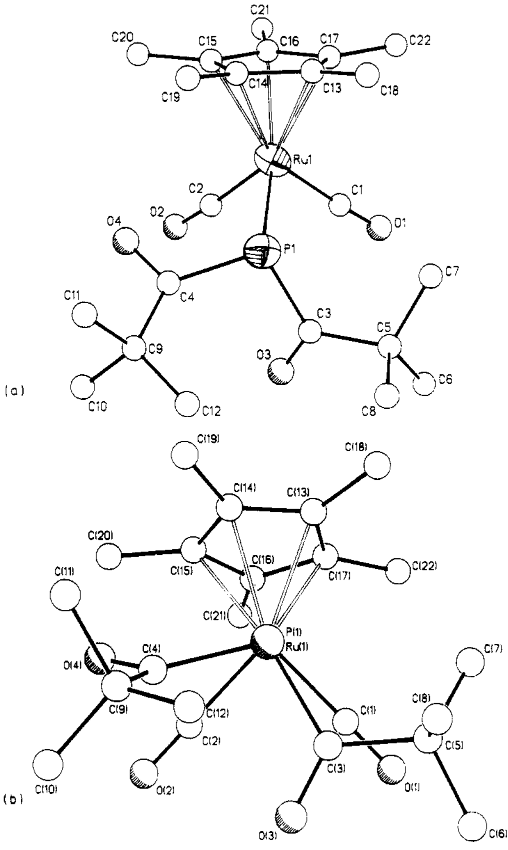


Figure 1. Two views of the molecular structure of $(\eta^5\text{-}C_5Me_5)(CO)_2RuP[C(O)(t\text{-}Bu)]_2$ (3). (b) approximates a Newman projection down the P(1)Ru(1) bond.

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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