ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2010, Vol. 36, No. 12, pp. 891–896. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © V.A. Milyukov, A.A. Zagidullin, E. Hey-Hawkins, O.G. Sinyashin, 2010, published in Koordinatsionnaya Khimiya, 2010, Vol. 36, No. 12, pp. 903–908.

Cycloaddition Reactions of 1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes in the Coordination Sphere of Tungsten Carbonyl

V. A. Milyukov[a], *, A. A. Zagidullin[a], E. Hey-Hawkins[b], and O. G. Sinyashin[a]

[a] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. akademika Arbuzova 8, Kazan, 420083 Tatarstan, Russia*

[b] *Institute of Inorganic Chemistry, Leipzig University, Johannisallee 29, 04103 Leipzig, Germany*

**E-mail: miluykov@iopc.knc.ru*

Received March 19, 2010

Abstract—1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes react with tungsten hexacarbonyl under the conditions of “indirect” replacement of the carbonyl group to give 1 : 1 complexes; [4+2] cycloaddition reactions of these complexes with maleic acid derivatives and substituted acetylenes afford tungsten carbonyl complexes containing 10-alkyl-1,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-diones and 1-alkyl-2,3-diphenylphosphirenes, respectively.

DOI: 10.1134/S1070328410120043

Transition metal complexes with 1-alkyl(aryl)phosphacyclopenta-2,4-dienes (phospholes) fix the attention of researchers because they allow a series of chemical transformations that are unknown with free phospholes. For instance, heating or irradiation of a mixture of M(CO)$_6$ (M = Cr, Mo, or W) and 1-phenylphosphole gives complexes containing dimeric diphosphole as a ligand (this dimer results from a [2+2] cycloaddition, which is not typical of free 1*R*-phospholes) [1]. Dimerization of phospholes in [2+2], [4+2], and [4+4] cycloaddition reactions has also been observed in the coordination spheres of other metals: nickel [2, 3], platinum [4], palladium [5], and ruthenium [6–8]. Intramolecular reactions of 1-phenylphospholes with vinylphosphines [9–12], 2-vinylpyridine [13], phenyl vinyl sulfoxide [14], and ethyl vinyl ketone [15] in the coordination spheres of ruthenium or palladium compounds have been employed for the template synthesis of chiral bidentate ligands. In addition, 7-phosphanorbornadienes obtained by [4+2] cycloaddition reactions of a tungsten complex with 1-phenylphosphole and dimethyl acetylenedicarboxylate have been successfully used to generate highly reactive phosphorus species, namely, phosphinidenes, which are the phosphorus analogs of carbenes [16–18].

It should be noted that the complexing properties of phospholes substantially depend on the number of P atoms in the ring since sequential replacement of the CR fragment by a phosphorus atom enhances the aromaticity of phospholes [19]. For instance, 1-[bis(trimethylsilyl)methyl]-3,5-di-*tert*-butyl-1,2,4-triphosphole reacts with transition metal compounds to give complexes with η^1- [20], η^4- [21], or η^5-type of coordination [22], depending on the metal nature.

The goal of this study was to examine the complexing properties of 1-alkyl-1,2-diphosphacyclopenta-2,4-dienes (**I**) in reactions with tungsten carbonyl, to identify the types of coordination in the resulting complexes, and to study their reactivities toward various dienophiles (maleic acid derivatives and substituted acetylenes).

EXPERIMENTAL

All manipulations dealing with the preparation of the starting reagents and the synthesis and isolation of products were carried out under an inert gas in a standard Schlenk vessel. All solvents were distilled over Na/benzophenone immediately before use. NMR spectra were recorded for 10–20% solutions in inert solvents (C_6D_6 and $CDCl_3$) on a Bruker MSL-400 spectrometer (400 (^{1}H), 161.97 (^{31}P), and 100.6 MHz (^{13}C)) with tetramethylsilane as the internal standard (^{1}H, ^{13}C) and with 85% H_3PO_4 as the external standard (^{31}P). IR spectra were recorded on a Bruker Vector-22 FTIR pulse spectrometer in the 400–4000 cm^{-1} range.

Commercial reagents (tungsten hexacarbonyl, maleic anhydride, maleimide, dimethyl acetylenedicarboxylate, and diphenylacetylene) were used without preliminary purification. 1-Alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes were prepared as described in [23].

Synthesis of (1-R-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene)pentacarbonyltungsten

Elemental analysis data, melting temperatures, and yields of complexes **II–IV***

Complex (empirical formula)	T_m, °C	Yield, g (%)	Content (found/calculated), %		
			C	H	P
IIa ($C_{28}H_{20}O_5P_2W$)	128	0.61 (89)	49.01 (49.29)	3.23 (2.95)	9.19 (9.08)
IIb ($C_{30}H_{24}O_5P_2W$)	130	0.64 (90)	50.34 (50.73)	4.13 (3.41)	8.99 (8.72)
IIc ($C_{30}H_{24}O_5P_2W$)	130	0.64 (91)	50.54 (50.73)	4.17 (3.41)	8.87 (8.72)
IIIa ($C_{32}H_{22}O_8P_2W$)	142	0.32 (80)	49.12 (49.26)	2.45 (2.84)	7.77 (7.94)
IIIb ($C_{34}H_{26}O_8P_2W$)	150	0.33 (80)	50.32 (50.52)	3.36 (3.24)	7.48 (7.66)
IIIc ($C_{34}H_{26}O_8P_2W$)	153	0.34 (83)	50.28 (50.52)	3.16 (3.24)	7.29 (7.66)
IVa ($C_{32}H_{23}NO_7P_2W$)	144	0.32 (82)	49.14 (49.32)	2.56 (2.97)	7.45 (7.95)
IVb ($C_{34}H_{27}NO_7P_2W$)	152	0.35 (86)	50.39 (50.58)	3.18 (3.37)	7.39 (7.67)
IVc ($C_{34}H_{27}NO_7P_2W$)	155	0.34 (84)	50.44 (50.58)	3.22 (3.37)	7.59 (7.67)

* Complexes **IIa–IIc** are dark red powders; complexes **IIIa–IIIc** and **IVa–IVc** are yellow powders.

(R = Et (IIa), Bu (IIb), and *iso*-Bu (IIc)). A solution of tungsten hexacarbonyl (0.35 g, 1 mmol) in THF (100 ml) was exposed to UV light in a quartz reaction vessel under argon at 5°C for 3 h. The resulting solution was lemon-colored. A solution of 1-R-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-diene (1 mmol) in THF (10 ml) was added and the reaction mixture was stirred for 12 h. The solvent was removed in vacuo and the product was extracted with hexane. The elemental analysis data, melting temperatures, and yields of complexes **II** are given in table.

IIa (R = Et).

^{1}H NMR (C_6D_6, δ, ppm): 1.14 dt (3H, CH_3, $^3J_{HH}$ = 7.14 Hz, $^3J_{HP}$ = 13.1 Hz), 2.13 m (2H, CH_2), 7.34 d (Ph, $^3J_{HP}$ = 7.12 Hz), 6.96 t (4H, Ph, $^3J_{HP}$ = 6.12 Hz), 7.00 d (4H, Ph, $^3J_{HP}$ = 4.81 Hz), 7.03 d (2H, Ph, $^3J_{HP}$ = 5.82 Hz), 7.07 d (4H, Ph, $^3J_{HP}$ = 7.13 Hz), 7.23 d (2H, Ph, $^3J_{HP}$ = 5.13 Hz), 7.31 t (1H, Ph, $^3J_{HP}$ = 8.49 Hz).

^{31}P NMR (C_6D_6, δ, ppm): 209.56 d ($^1J_{PP}$ = 241.3 Hz, $^2J_{PW}$ = 279.2 Hz), 36.55 d ($^1J_{PP}$ = 241.3 Hz, $^1J_{PW}$ = 212.3 Hz).

^{13}C NMR (C_6D_6, δ, ppm): 152.12 t ($^2J_{CP}$ = 13.14 Hz), 161.14 dd ($^2J_{CP}$ = 10.34 Hz, $^2J_{CP}$ = 4.87 Hz), 189.93 dd ($^2J_{CP}$ = 51.12 Hz, $^2J_{CP}$ = 14.99 Hz).

IR (hexane, ν(CO), cm^{-1}): 1945, 2023, 2124, 2146.

IIb (R = Bu).

^{1}H NMR (C_6D_6, δ, ppm): 0.64 t (3H, CH_3, $^3J_{HH}$ = 7.09 Hz), 0.77 m (2H, CH_2), 1.04 m (2H, CH_2), 1.71 m (2H, CH_2), 6.9–7.8 m (15H, Ph).

^{31}P NMR (C_6D_6, δ, ppm): 213.47 d ($^1J_{PP}$ = 234.3 Hz, $^2J_{PW}$ = 268.14 Hz), 48.37 d ($^1J_{PP}$ = 234.3 Hz, $^1J_{PW}$ = 210.36 Hz).

^{13}C NMR (C_6D_6, δ, ppm): 148.77 t ($^3J_{CP}$ = 13.34 Hz), 165.99 dd ($^3J_{CP}$ = 7.12 Hz, $^3J_{CP}$ = 2.10 Hz), 193.21 dd ($^3J_{CP}$ = 51.07 Hz, $^3J_{CP}$ = 12.02 Hz).

IR (hexane,ν(CO), cm^{-1}): 1932, 2070, 2134, 2145.

IIc (R = *iso*-Bu).

^{1}H NMR (C_6D_6, δ, ppm): 0.92 d (6H, CH_3, $^3J_{HH}$ = 6.23 Hz), 1.14 m (1H, CH), 1.72 m (2H, CH_2), 6.9–7.8 m (15H, Ph).

^{31}P NMR (C_6D_6, δ, ppm): 208.31 d ($^{1}J_{PP}$ = 246.3 Hz, $^{2}J_{PW}$ = 271.2 Hz), 33.13 d ($^{1}J_{PP}$ = 246.3 Hz, $^{1}J_{PW}$ = 203.1 Hz).

^{13}C NMR (C_6D_6, δ, ppm): 149.77 t ($^{3}J_{CP}$ = 13.34 Hz), 164.99 dd ($^{3}J_{CP}$ = 7.12 Hz, $^{3}J_{CP}$ = 2.10 Hz), 188.99 dd ($^{3}J_{CP}$ = 51.07 Hz, $^{3}J_{CP}$ = 12.02 Hz).

IR (hexane, ν(CO), cm^{-1}): 1933, 2072, 2163, 2178.

Reactions of 1-R-1,2-diphosphole complexes II with maleic acid derivatives. A solution of complex **II** (1 mmol) and a maleic acid derivative (1 mmol) in toluene (20 ml) was heated at 100°C for 3 h. On cooling, the solution was filtered and concentrated in vacuo to a small volume (5 ml). Hexane (30 ml) was added and the resulting precipitate was filtered off and dried in vacuo. The complexes obtained were pentacarbonyl(10-R-7,8,9-triphenyl-4-oxa-1,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-dione)tungsten (R = Et (**IIIa**), Bu (**IIIb**), and *iso*-Bu (**IIIc**)) and pentacarbonyl(10-R-7,8,9-triphenyl-4-aza-1,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-dione)tungsten (R = Et (**IVa**), Bu (**IVb**), and *iso*-Bu (**IVc**)). The elemental analysis data, melting temperatures, and yields of complexes **III** and **IV** are given in table.

IIIa (R = Et; maleic anhydride).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.9 dt (3H, CH_3, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HP}$ = 15.08 Hz), 1.28 ddq (2H, CH_2, $^{3}J_{HH}$ = 7.9 Hz, $^{2}J_{HP}$ = 51.9 Hz, $^{3}J_{HP}$ = 1.8 Hz), 4.31 dd (1H, CH, $^{3}J_{HP}$ = 8.0 Hz, $^{2}J_{HP}$ = 9.9 Hz), 4.79 d (1H, CH, $^{3}J_{HP}$ = 8.80 Hz), 6.72 d (2H, Ph, $^{3}J_{HH}$ = 6.85 Hz), 6.87 t (2H, Ph, $^{3}J_{HH}$ = 7.34 Hz), 6.89 d (1H, Ph, $^{3}J_{HH}$ = 6.85 Hz), 7.01 m (3H, Ph), 7.12 m (5H, Ph), 7.23 d (3H, Ph, $^{3}J_{HH}$ = 5.87 Hz), 7.37 d (2H, Ph, $^{3}J_{HH}$ = 6.85 Hz).

^{31}P NMR ($CDCl_3$, δ, ppm): 82.04 d ($^{1}J_{PP}$ = 201.5 Hz), 3.4 d ($^{1}J_{PP}$ = 201.5 Hz, $^{1}J_{PW}$ = 253.3 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 76.86 dd ($^{1}J_{CP}$ = 26.47 Hz, $^{1}J_{CP}$ = 4.14 Hz), 140.91 dd ($^{1}J_{CP}$ = 27.50 Hz, $^{2}J_{CP}$ = 18.40 Hz), 158.13 dd ($^{2}J_{CP}$ = 17.99 Hz, $^{2}J_{CP}$ = 3.93 Hz), 169.19 s (CO), 171.55 s (CO).

IIIb (R = Bu; maleic anhydride).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.78 t (3H, CH_3, $^{3}J_{HH}$ = 6.85 Hz), 0.82 m (2H, CH_2), 1.14 m (2H, CH_2), 1.78 m (2H, CH_2), 4.49 dd (CH, $^{3}J_{HH}$ = 8.80 Hz, $^{2}J_{HP}$ = 25.43 Hz), 4.73 d (CH, $^{3}J_{HH}$ = 8.34 Hz), 6.8–7.5 m (15H, Ph).

^{31}P NMR ($CDCl_3$, δ, ppm): 86.45 d ($^{1}J_{PP}$ = 203.0 Hz), 9.79 d ($^{1}J_{PP}$ = 203.0 Hz, $^{1}J_{PW}$ = 254.81 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 73.14 d (C–Ph, $^{1}J_{CP}$ = 27.71 Hz), 167.48 dd ($^{1}J_{CP}$ = 27.91 Hz, $^{2}J_{CP}$ = 18.40 Hz), 170.39 dd ($^{2}J_{CP}$ = 18.19 Hz, $^{2}J_{CP}$ = 4.14 Hz), 194.33 d (CO, $^{2}J_{CP}$ = 10.62 Hz), 194.81 d (CO, $^{3}J_{CP}$ = 6.20 Hz).

IIIc (R = *iso*-Bu; maleic anhydride).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.71 d (3H, CH_3, $^{3}J_{HH}$ = 6.85 Hz), 0.78 d (3H, CH_3, $^{3}J_{HH}$ = 6.85 Hz), 1.8 m (1H, CH), 1.95 m (2H, CH_2), 4.40 dd (CH, $^{3}J_{HH}$ = 8.80 Hz, $^{2}J_{HP}$ = 10.27 Hz), 4.65 d (CH, $^{3}J_{HH}$ = 8.80 Hz), 6.68 d (2H, Ph, $^{3}J_{HH}$ = 6.85 Hz), 6.82 t (3H, Ph, $^{3}J_{HH}$ = 7.09 Hz), 6.87 d (2H, Ph, $^{3}J_{HH}$ = 7.34 Hz), 6.93–7.09 m (3H, Ph), 7.15 d (3H, Ph, $^{3}J_{HH}$ = 9.29 Hz), 7.34 d (2H, Ph, $^{3}J_{HH}$ = 6.85 Hz).

^{31}P NMR ($CDCl_3$, δ, ppm): 80.12 d ($^{1}J_{PP}$ = 207.1 Hz), 1.7 d ($^{1}J_{PP}$ = 207.1 Hz, $^{1}J_{PW}$ = 259.3 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 77.01 dd (C–Ph, $^{1}J_{CP}$ = 26.26 Hz, $^{2}J_{CP}$ = 4.14 Hz), 141.48 dd ($^{1}J_{CP}$ = 27.91 Hz, $^{2}J_{CP}$ = 18.40 Hz), 157.99 dd ($^{2}J_{CP}$ = 18.19 Hz, $^{2}J_{CP}$ = 4.14 Hz), 169.23 s (CO), 171.53 s (CO).

IVa (R = Et; maleimide).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.72 dt (3H, CH_3, $^{3}J_{HH}$ = 7.82 Hz, $^{3}J_{HP}$ = 16.44 Hz), 1.32 ddq (2H, CH_2, $^{3}J_{HH}$ = 7.82 Hz, $^{2}J_{HP}$ = 49.16 Hz, $^{3}J_{HP}$ = 1.46 Hz), 4.24 dd (1H, CH, $^{3}J_{HH}$ = 7.38 Hz, $^{2}J_{HP}$ = 10.99 Hz), 4.57 d (1H, CH, $^{3}J_{HH}$ = 7.38 Hz), 6.16 d (4H, Ph, $^{3}J_{HH}$ = 9.12 Hz), 7.15 d (4H, Ph, $^{3}J_{HH}$ = 7.27 Hz), 7.07 d (4H, Ph, $^{3}J_{HH}$ = 6.82 Hz), 7.14 d (2H, Ph, $^{3}J_{HH}$ = 6.23 Hz), 7.36 d (1H, Ph, $^{3}J_{HH}$ = 6.77 Hz), 9.02 s (1H, NH).

^{31}P NMR ($CDCl_3$, δ, ppm): 81.45 d ($^{1}J_{PP}$ = 204.5 Hz), 3.0 d ($^{1}J_{PP}$ = 204.5 Hz, $^{1}J_{PW}$ = 251.7 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 74.85 dd (C–Ph, $^{1}J_{CP}$ = 24.32 Hz, $^{2}J_{CP}$ = 2.81 Hz), 140.98 dd (C=C, $^{1}J_{CP}$ = 27.72 Hz, $^{2}J_{CP}$ = 19.23 Hz), 157.97 dd (C=C, $^{2}J_{CP}$ = 18.31 Hz, $^{2}J_{CP}$ = 4.06 Hz), 174.89 s (CO), 177.99 s (CO).

IVb (R = Bu; maleimide).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.79 t (3H, CH_3, $^{3}J_{HH}$ = 6.85 Hz), 0.82 m (2H, CH_2), 1.13 m (2H, CH_2), 1.69 m (2H, CH_2), 4.50 dd (CH, $^{3}J_{HH}$ = 8.80 Hz, $^{2}J_{HP}$ = 25.43 Hz), 4.78 d (CH, $^{3}J_{HH}$ = 8.34 Hz), 6.75 d (5H, Ph, $^{3}J_{HH}$ = 9.29 Hz), 6.99 d (5H, Ph, $^{3}J_{HH}$ = 7.34 Hz), 7.07 d (5H, Ph, $^{3}J_{HH}$ = 6.85 Hz), 7.36 d (2H, Ph, $^{3}J_{HH}$ = 6.85 Hz), 9.02 s (1H, NH).

^{31}P NMR ($CDCl_3$, δ, ppm): 82.6 d ($^{1}J_{PP}$ = 214.5 Hz), 3.7 d ($^{1}J_{PP}$ = 214.5 Hz, $^{1}J_{PW}$ = 244.4 Hz).

^{13}C NMR ($CDCl_3$, δ, ppm): 73.14 d ($^{1}J_{CP}$ = 27.71 Hz), 165.48 dd ($^{1}J_{CP}$ = 27.91 Hz, $^{2}J_{CP}$ = 15.40 Hz), 172.39 dd ($^{2}J_{CP}$ = 18.19 Hz, $^{2}J_{CP}$ = 4.14 Hz), 189.33 d (CO, $^{2}J_{CP}$ = 10.62 Hz), 192.81 d (CO, $^{3}J_{CP}$ = 6.20 Hz).

IVc (R = *iso*-Bu; maleimide).

^{1}H NMR ($CDCl_3$, δ, ppm): 0.68 d (3H, CH_3, $^{3}J_{HH}$ = 6.85 Hz), 0.76 d (3H, CH_3, $^{3}J_{HH}$ = 6.85 Hz), 1.03 m (2H, CH_2), 1.48 m (1H, CH), 4.15 dd (1H, CH, $^{3}J_{HH}$ = 7.83 Hz, $^{2}J_{HP}$ = 10.27 Hz), 6.75 d (3H, Ph, $^{3}J_{HH}$ = 9.29 Hz), 6.99 d (4H, Ph, $^{3}J_{HH}$ = 7.34 Hz), 7.07 d (3H, Ph, $^{3}J_{HH}$ = 6.85 Hz), 7.14 d (3H, Ph, $^{3}J_{HH}$ = 6.36 Hz), 7.36 d (2H, Ph, $^{3}J_{HH}$ = 6.85 Hz), 9.05 s (1H, NH).

^{31}P NMR ($CDCl_3$, δ, ppm): 80.6 d ($^{1}J_{PP}$ = 212.2 Hz), 1.9 d ($^{1}J_{PP}$ = 212.2 Hz, $^{1}J_{PW}$ = 245.2 Hz).

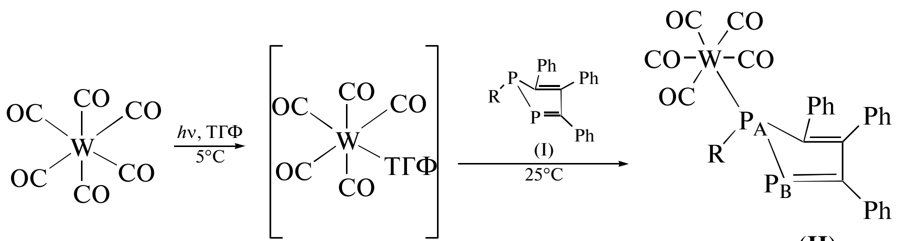
^{13}C NMR ($CDCl_3$, δ, ppm): 74.80 dd (C–Ph, $^{1}J_{CP}$ = 24.40 Hz, $^{2}J_{CP}$ = 2.89 Hz), 140.86 dd ($^{1}J_{CP}$ = 27.71 Hz, $^{2}J_{CP}$ = 19.02 Hz), 157.91 dd ($^{2}J_{CP}$ = 18.40 Hz, $^{2}J_{CP}$ = 4.34 Hz), 174.78 s (CO), 177.76 s (CO).

Reactions of complexes II with dimethyl acetylenedicarboxylate. A mixture of complex **IIb** (**IIc**) (0.71 g, 1 mmol), dimethyl acetylenedicarboxylate (0.14 g, 1 mmol), and an excess of diphenylacetylene (0.54 g, 3 mmol) was heated in toluene (50 ml) at 50°C for 3 h. The solution was filtered and concentrated to a small volume. The residue was analyzed using ^{31}P NMR spectroscopy. Along with a signal for phosphabenzene (**V**) at δ 213 ppm, the spectrum shows a singlet at δ –170 ppm for pentacarbonyl(1-ethyl-2,3-diphenylphosphirene)tungsten (**VIa**) or at δ –172 ppm for pentacarbonyl(1-isobutyl-2,3-diphenylphosphirene)tungsten (**VIb**), which agrees with the literature data [17].

RESULTS AND DISCUSSION

For the synthesis of complexes of 1-R-1,2-diphosphacyclopentadienes with $W(CO)_6$, we used “indirect” photochemical replacement of the carbonyl group. This technique involves irradiation of a solution of tungsten hexacarbonyl in THF with UV light; the resulting labile complex $W(CO)_5THF$ exists only in solution. Addition to the latter of an appropriate ligand allows irradiation-free replacement of the THF molecule to give monosubstituted carbonyl complexes of tungsten.

Complexes **II** were obtained as rufous powders in 89–91% yields.

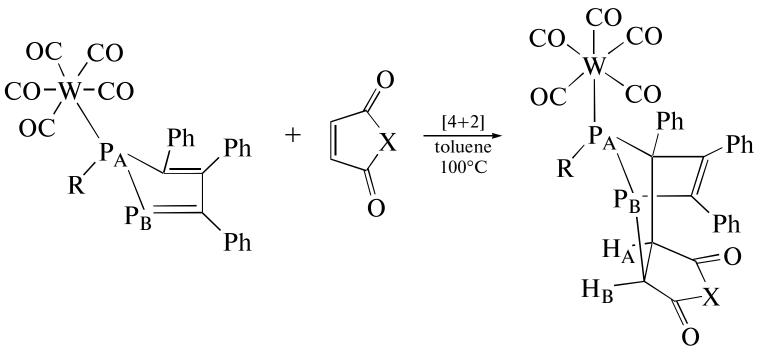


(II)

R = Et (a), Bu (b), *iso*-Bu (c)

The structures of complexes **II** were determined from IR and ^{1}H, 3^{1}P, and ^{13}C NMR spectra and confirmed by elemental analysis data. For instance, the ^{31}P{^{1}H} NMR spectrum of complex **IIc** shows two doublets at δ_P 208.3 and 33.1 ppm ($^1J_{PP} = 245$ Hz) for the P_B and P_A atoms, respectively. Note that a downfield shift by 29.7 ppm compared to the signals for the starting ligand (δ_P 207.5 and 62.8 ppm) is observed only for the P atom bearing the alkyl group, which points to the coordination of tungsten through the P_A atom only. It should be noted that in complex **IIc**, the geminal coupling constant $^2J_{WP} = 271.11$ Hz is higher than the direct constant $^1J_{WP} = 203$ Hz, thus suggesting hyperconjugation in 1-R-1,2-diphosphole complexes **II**. In the ^{13}C NMR spectrum, the signal for the carbon atom at the P_B=C bond appears as a doublet of doublets because of the couplings with two nonequivalent P nuclei.

The coordination of the tungsten atom through the P_A atom was confirmed by the chemical behavior of complexes **II** in cycloaddition reactions:

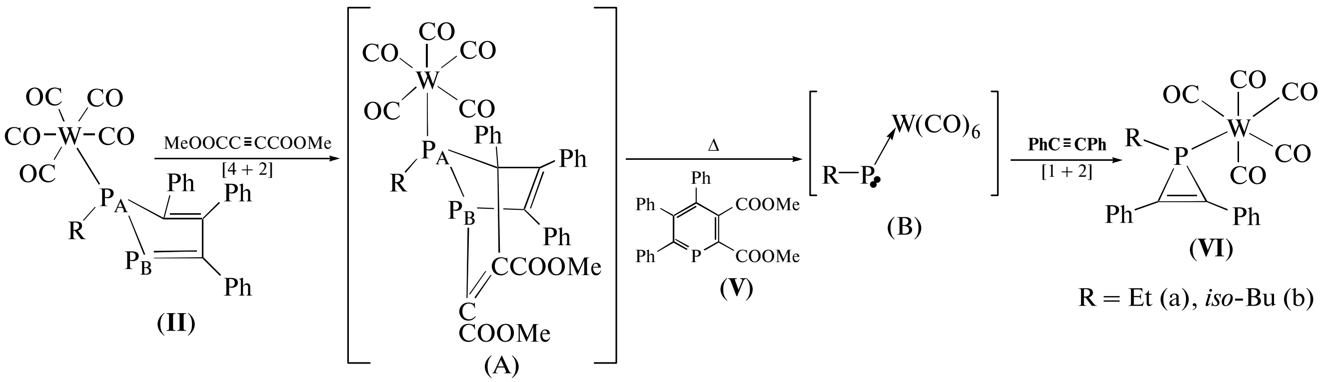


III: X = O, R = Et (a), Bu (b) *iso*-Bu (c)
IV: X = NH, R = Et (a), Bu (b) *изо*-Bu (c)

We found that complexes **II** react with maleic anhydride and maleimide in hot toluene to give the corresponding [4+2] cycloadducts **III** and **IV**, which were isolated as yellow powders in high yields (80–85%). The $^{31}P\{^1H\}$ NMR spectrum of complex **IIIc** shows two doublets at δ_P 82.4 and 3.4 ppm with a coupling constant of 201.5 Hz. For the P–W bond, the coupling constant is observed only for the P_A atom ($^1J_{WP}$ = 253.3 Hz) directly attached to the tungsten atom. This suggests the absence of hyperconjugation in complexes **III** and **IV**. In the ^{13}C NMR spectrum of complex **IIIc**, the signals for the carbon atoms at the C=C double bond appear as two doublets of doublets at δ_C = 141.1 and 159.0 ppm because of the couplings with two nonequivalent P nuclei.

In [23], we have demonstrated that reactions of free 1-R-1,2-diphospholes (**I**) with maleic acid derivatives also follow the [4+2] cycloaddition pattern with high regio- and stereoselectivity. The reaction produces only one diastereoisomer as two enantiomers, which seems to be the case of complexes **III** and **IV**.

It was interesting to carry out [4+2] cycloaddition reactions of complexes **II** with substituted acetylenes. In our opinion, the easier cleavage of the P–P bond compared to the P–C one will allow generation of alkylphosphinidene complexes under milder conditions than with monophospholes (110°C). We found that heating of tungsten complexes **II** with dimethyl acetylenedicarboxylate and diphenylacetylene at 50°C gives complexes **VI** with 1-alkyl-2,3-diphenylphosphirenes as ligands.



R = Et (a), *iso*-Bu (b)

Apparently, the first step involves [4+2] cycloaddition leading to an unstable intermediate (**A**). Cleavage of the P–P and P–C bonds in complex **A** results in the formation of phosphabenzene (**V**) and an alkylphosphinidene complex (**B**), which is "trapped" by diphenylacetylene to form a tungsten complex with diphenylphosphirene (**VI**). The $^{31}P\ \{^1H\}$ NMR spectrum shows a signal for phosphabenzene **V** (δ 213 ppm) together with a signal for complex **VI** at δ –170 ppm, which fully agrees with the previous data for this complex [17].

Thus, we found that tungsten(II) carbonyl complexes **II** with 1-alkyl-3,4,5-triphenyl-1,2-diphosphacyclopenta-2,4-dienes as ligands react with maleic acid derivatives and diphenylacetylene according to the [4+2] cycloaddition pattern to give tungsten complexes containing 10-alkyl-1,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-8-ene-3,5-diones (**III**, **IV**) and 1-alkyl-2,3-diphenylphosphirenes (**VI**), respectively.

REFERENCES

1. Santini, C.C., Fischer, J., Mathey F., and Mitschler A, *J. Am. Chem. Soc.,* 1980, vol. 102, no. 18, p. 5809.
2. Mercier, F., Mathey, F., Fischer, J., and Nelson, J., *J. Am. Chem. Soc.*, 1984, vol. 106, no. 2, p. 425.
3. Mercier, F., Mathey, F., Fischer, J., and Nelson, J., *Inorg. Chem.*, 1985, vol. 24, no. 24, p. 4141.
4. Wilson, W.L., Rahn, J.A., Alcock, N.W., et al., *Inorg. Chem.*, 1994, vol. 33, no. 1, p. 109.
5. Wilson, W.L., Fischer, J., Wasylishen, R.E., et al., *Inorg. Chem.,* 1996, vol. 35, no. 6, p. 1486.
6. Redwine, K.D. and Nelson, J.H., *Organometallics*, 2000, vol. 19, no. 16, p. 3054.
7. Barthel-Rosa, L.P., Nelson, J.H., Catalano, V.J., and Fischer, J., *Phosphorus, Sulfur, Silicon, Relat. Elem.*, 1996, vol. 109, nos. 1-4, p. 169.
8. Ji, H.L., Nelson, J.H., DeCian, A., et al., *J. Organomet. Chem.,* 1997, vol. 529, nos. 1-2, p. 395.
9. Redwine, K.D. and Nelson, J.H., *J. Organomet. Chem.,* 2000, vol. 613, no. 2, p. 177.
10. Green, R.L., Nelson, J.H., and Fischer, J., *Organometallics*, 1987, vol. 6, no. 10, p. 2256.
11. Ji, H.L., Nelson, J.H., and Cian, A. De, et al., *Organometallics*, 1992, vol. 11, no. 5, p. 1840.
12. Ghebreyessus, K.Y., Gul, N., and Nelson, J.H., *Organometallics*, 2003, vol. 22, no. 14, p. 2977.

13. Kessler, J.M., Nelson, J.H., Fischer, J., et al., *Inorg. Chem.*, 1994, vol. 33, no. 19, p. 4319.
14. Siah, S.Y., Leung, P.H., and Mok, K.F., *Chem. Commun.*, 1995, no. 17, p. 1747.
15. Yongxin, L., Selvaratnam, S., Jagadese, J.V., and Leung, P.H., *Inorg. Chem.*, 2003, vol. 42, no. 10, p. 3229.
16. Marinetti, A. and Mathey, F., *Organometallics*, 1984, vol. 3, no. 3, p. 456.
17. Marinetti, A., Mathey, F., Fischer, J., and Mitschler, A., *J. Am. Chem. Soc.*, 1982, vol. 104, no. 16, p. 4484.
18. Marinetti, A., Mathey, F., Fischer, J., and Mitschler, A, *J. Chem. Soc., Chem. Commun.*, 1984, no. 1, p. 45.
19. Nyulaszi, L., *J. Phys. Chem.*, 1996, vol. 100, no. 15, p. 6194.
20. Caliman, V., Hitchcock, P.B., and Nixon, J.F., *J. Chem. Soc., Chem. Commun.*, 1995, no. 16, p. 1661.
21. Hitchcock, P.B., Nixon, J.F., and Sakarya, N., *J. Chem. Soc., Chem. Commun.,* 1996, no. 24, p. 2751.
22. Caliman, V., Hitchcock, P.B., and Nixon, J.F., *J. Chem. Soc., Chem. Commun.*, 1997, no. 14, p. 1305.
23. Miluykov, V., Bezkishko, I., Zagidullin, A., et al., *Eur. J. Org. Chem.*, 2009, no. 8, p. 1269.