10. S. P. Gromov, A. I. Vedernikov, and O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 950 [*Russ. Chem. Bull.*, 1995, **44**, 923 (Engl. Transl.)].

11. S. P. Gromov, A. I. Vedernikov, and O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 687 [*Russ. Chem. Bull.*, 1996, **45**, 648 (Engl. Transl.)].

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Coupling of dehydrobenzene, CO, and an enyne on an Ru$_3$ cluster. Crystal structure of the complex $\mathrm{Ru_3(CO)_6\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(Ph){=}CH\overline{C C(Ph)(1,2\text{-}C_6H_4)C}({=}O)\}}$

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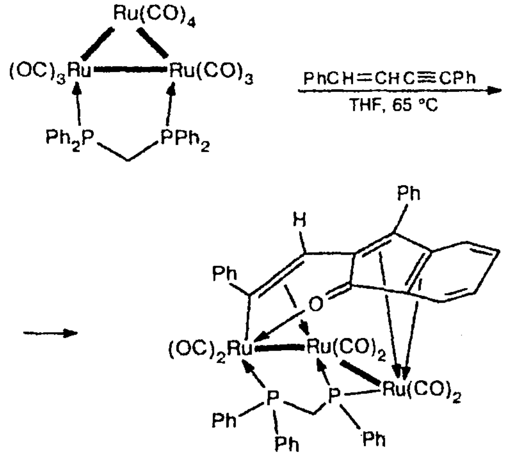
Continuing the study of transformations of enynes on Ru$_3$-carbonyl clusters,[1] we carried out the thermal reaction of the Ru$_3$(CO)$_{10}$(μ-dppm) cluster (dppm = Ph$_2$PCH$_2$PPh$_2$) with PhC≡CCH=CHPh and obtained the red complex $\mathrm{Ru_3(CO)_6\{\mu_3\text{-}P(Ph)CH_2PPh_2\}\{\mu_3\text{-}C(Ph){=}CH\overline{C C(Ph)(1,2\text{-}C_6H_4)C}({=}O)\}}$ (**1**) in ~20% yield.



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The ^{1}H NMR spectrum (CDCl$_3$, 25 °C) of complex **1** contains a complex multiplet from 29 aromatic protons in the region of δ 6.6—8.2, a signal for the olefinic hydrogen atom at δ 5.60 (dd, 1 H, J = 7.3 Hz, J = 2.5 Hz), and two signals for the methylene protons at δ 4.38 (ddd, 1 H) and 4.68 (ddd, 1 H). The ^{31}P NMR spectrum exhibits two doublet signals at δ 210.3 and 16.5 with splitting J_{PP} = 24.8 Hz, which indicates the transformation of the dppm ligand into the phosphido-phosphine ligand during the formation of complex **1**.

The IR spectrum (CH$_2$Cl$_2$) showed the presence of terminal CO groups (ν(CO)/cm^{-1}: 2030 m, 2005 s, 1983 s, 1973 sh, 1941 m, and 1921 m), and weak absorption at 1533 cm^{-1} characteristic of the ketone group coordinated with the metal atom[2] was also observed.

According to the X-ray diffraction analysis data, the crystals of complex **1** are monoclinic, at T = 293 K a = 14.672(6) Å, b = 20.397(6) Å, c = 15.551(5) Å, β = 104.54(3)°, V = 4505(3) Å^3, Z = 4, d_{calc} = 1.672 g cm^{-3}, space group $P2_1n$, 12022 independent reflections, R_1 = 0.0595 for 7761 observed reflections with I = 2σ(I), three ruthenium atoms are arranged in an open fashion (the Ru(1)—Ru(2) and Ru(2)—Ru(3) bond lengths are equal to 2.778(1) and 3.028(1) Å, respectively; the Ru(1)—Ru(2)—Ru(3) angle is equal to 102.09(3)°, and the nonbonding Ru(1)...Ru(3) distance is equal to 4.517(1) Å), and each ruthenium atom coordinates two terminal CO groups (Fig. 1). The complex organic ligand bound to three ruthenium atoms is formed upon coupling of dehydrobenzene (derived from dppm), CO, and metallated enyne and can be considered as an indenone derivative (one of the ethylene hydrogen atoms of the starting enyne is replaced by the Ru(1) atom, and the second hydrogen atom is at C(8)). The Ru(1) atom forms a σ-bond with the ethylenic C(7) atom with a distance of 2.070(5) Å; the same atom coordinates the oxygen atom of the ketone group (Ru(1)—O(7) 2.133(3) Å) and phosphinic P(1) atom of the phosphido-phosphine ligand (Ru(1)—P(1) 2.410(1) Å). The phosphidic P(2) atom serves as a bridge between the Ru(2) and

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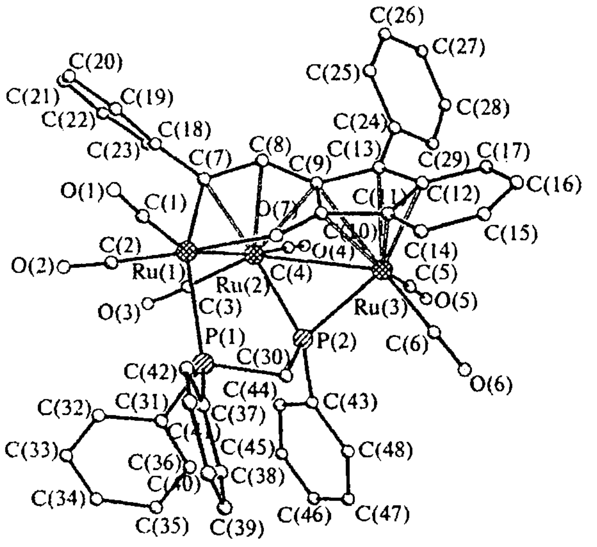

Fig. 1. Molecular structure of complex **1**.

Ru(3) atoms, which form with the organic ligand the η^2-ethylenic (Ru(2)—C(7) 2.275(4) Å, Ru(2)—C(8) 2.209(4) Å) and η^4-dienic bonds (Ru(3)—C(9) 2.426(4) Å, Ru(3)—C(13) 2.263(5) Å, Ru(3)—C(12) 2.285(5) Å, and Ru(3)—C(11) 2.342(5) Å), respectively. In this consideration of bonding of the organic ligand with the metallic framework and taking into account the additional ligand environment, each Ru atom in complex **1** acquires the 18-electron shell. At the same time, weak interactions between the C(9) and Ru(2) atoms (2.446(4) Å) and the carbonyl C(10) and Ru(3) atoms (2.472(4) Å) are observed. The distance of the ketone C(10)—O(7) group in **1** equal to 1.263(5) Å is somewhat longer than that found for the cyclopentadienone $Ru(CO)_3(C_4Ph_4CO)$ complex[3] (1.224(4) Å) and is similar to that observed in the dimeric $[Ru(CO)_2(C_4Ph_4CO)]_2$ complex[2] (1.270(7) Å) with the bridging cyclopentadienone ligand with the >C=O→Ru bond. By contrast, in another complex with the bridging C_4Ph_4CO ligand, $Mo_2(CO)_3(\mu\text{-}C_2Ph_2)(\mu\text{-}C_4Ph_4CO)(\eta\text{-}C_4Ph_4)$,[4] for which η^5-coordination of the C_4Ph_4CO ligand is assumed, the >C=O bond is much longer (1.38(2) Å) and virtually coincides with the length of the exocyclic C—O bond (1.362(3) Å) in the ruthenium hydroxycyclopentadienyl $Ru(CO)_2(\eta^1\text{-}COMe)\{\eta^5\text{-}C_5H_2(SiMe_3)_2OH\}$ complex.[5]

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References

1. A. A. Koridze, V. I. Zdanovich, V. Yu. Lagunova, M. G. Ezernitskaya, P. V. Petrovskii, F. M. Dolgushin, and A. I. Yanovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1017 [*Russ. Chem. Bull.*, 1998, **47**, 988 (Engl. Transl.)].
2. M. J. Mays, M. J. Morris, P. R. Raithby, Y. Shvo, and D. Czarkie, *Organometallics*, 1989, **8**, 1162.
3. Y. Blum, Y. Shvo, and D. F. Chodosh, *Inorg. Chim. Acta*, 1985, **97**, L25.
4. J. A. Potenza, R. J. Johnson, R. Chirico, and A. Efraty, *Inorg. Chem.*, 1977, **16**, 2354.
5. A. A. Koridze, T. T. Efremidze, Yu. T. Struchkov, and A. I. Yanovsky, *Metalloorg. Khim.*, 1988, **1**, 826 [*J. Organomet. Chem. USSR*, 1988, **1**, 458 (Engl. Transl.)].

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