Letters to the Editor

Reaction of 3-(*N*-phenylamino)-1-*p*-tolylprop-2-en-1-one with $Ru_3(CO)_{12}$

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The reactivity of substituted oxadienes in reactions with $Ru_3(CO)_{12}$ was studied for 3-(*N*-phenylamino)-1-*p*-tolylprop-2-en-1-one $PhNHCH{=}CHCOC_6H_4Me$ (**1**) as a substrate. This compound contains a strong π-electron-releasing amino group on the one side of the double bond and an electron-withdrawing carbonyl group on the other. Earlier, the reactions of $Ru_3(CO)_{12}$ with unsaturated alkyl and aryl ketones were known to afford complexes, in which the main structural fragments are five-membered oxaruthenacycles additionally η^3-coordinated by other ruthenium atoms.[1,2]

The reaction of ketone **1** with $Ru_3(CO)_{12}$ was carried out in boiling hexane for 5 h. Chromatography of the reaction mixture gave three isomeric *cis*-dicarbonyl ruthenium complexes each containing two six-membered azaoxaruthenacycles, namely, dicarbonylruthenium bis[1-phenyl-4-(*p*-tolyl)-1-azabuta-1,3-dien-5-olates] (**2a**, **2b**, and **2c**) in 30, 10 and 4% yields, respectively (Scheme 1).

Complex **2a**, decomp. 180 °C. Found (%): C, 64.73; H, 4.42; N, 4.41. $C_{34}H_{28}N_2O_4Ru$. Calculated (%): C, 64.86; H, 4.45; N, 4.45. The structure of complex **2a** was determined by X-ray diffraction analysis (Fig. 1). Crystals **2a** ($C_{34}H_{28}N_2O_4Ru$) are triclinic, space group $P\bar{1}$, at 293 K a = 9.871(2) Å, b = 10.473(2) Å, c = 14.941(3) Å, α = 81.34(3)°, β = 77.99(3)°, γ = 78.71(3)°, V = 1466.7(5) Å^3, Z = 2, M = 629.65, d_{calc} = 1.426 g cm^{-3}. Final discrepancy factors were $R_1 = 0.0338$ (based on F for 4403 observed reflections with $I > 2\sigma(I)$) and $wR_2 = 0.07798$ (based on F^2 for all 6393 independent reflections). The Ru atom closes two six-membered azaoxaruthenacycles and is coordinated to two *cis*-carbonyl ligands. Both chelate ring are nearly planar (the metal atom deviates only slightly from the mean-square plane of the other atoms in each ring; the folding angles with respect to the O(3)...N(1) and O(4)...N(2) lines are 9.1° and 10.7°, respectively) and characterized by equalized bond lengths in the organic chain. The dihedral angle between the mean-square planes of the chelate rings is 73.7°. The octahedral environment of the Ru atom is characterized by transoid arrangement of the N atoms, while the carbonyl ligands are *trans* to the O atoms of the chelate rings. The IR and ^{1}H NMR data for complex **2a** are consistent with the X-ray diffraction data. Thus, the IR spectrum of complex **2a** shows two well-resolved intense CO absorption bands characteristic of a

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† Deceased.

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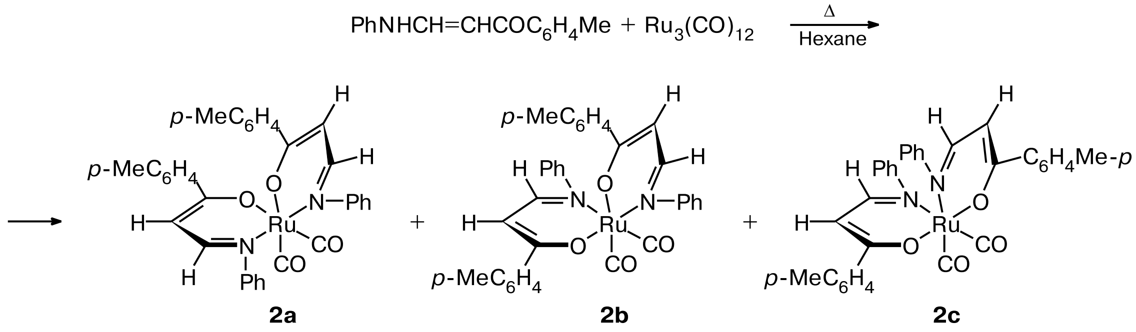
Scheme 1



cis-M(CO)$_2$ group (heptane, ν(CO)/cm^{-1}: 2046 vs, 1980 vs). Close IR data for a related ruthenium complex obtained by the reaction of Ru$_3$(CO)$_{12}$ with *N*-phenylsalicylidenimine have been reported earlier.[3] The ^{1}H NMR spectrum of complex **2a** contains one set of signals for the protons of two six-membered azaoxaruthenacycles, which suggests its molecular symmetry. Complex **2a**: ^{1}H NMR (CDCl$_3$), δ: 2.34 (s, 6 H, 2 Me); 5.76 (d, 2 H, J = 7 Hz); 7.15 (d, 4 H, C$_6\underline{H}_4$Me, J = 8 Hz); 7.25—7.32 (m, 10 H, 2 Ph); 7.42 (d, 2 H, J = 7 Hz); 7.82 (d, 4 H, C$_6\underline{H}_4$Me, J = 8 Hz).

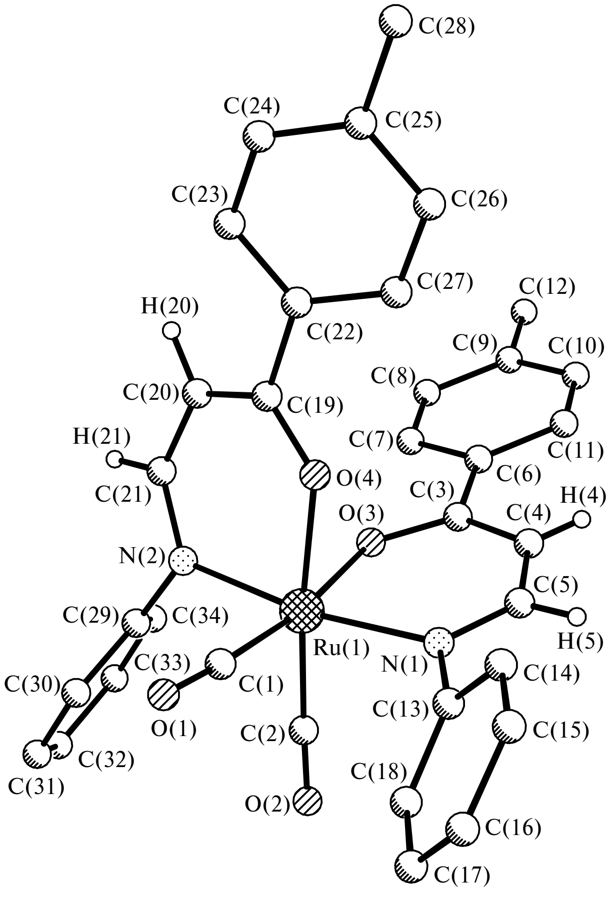


Fig. 1. Molecular structure of complex **2a**.

The structures of complexes **2b** and **2c** were determined from elemental analysis data and IR and ^{1}H NMR spectra; the X-ray diffraction data for complex **2a** were also useful. Complex **2b** was found to be chiral. One chelate ring in complex **2b** has a different spatial orientation, which correspondingly changes its IR and ^{1}H NMR spectra. The IR spectrum of complex **2b** shows two intense CO absorption bands characteristic of a *cis*-M(CO)$_2$ group (heptane, ν(CO)/cm^{-1}: 2042 vs, 1974 sh, 1960 vs). Close IR data for a related ruthenium complex obtained by the reaction of Ru$_3$(CO)$_{12}$ with *N,N*′-bis(salicylidene)ethylenediamine have been reported earlier.[4]

Complex **2b**, decomp. 195 °C. Found (%): C, 64.62; H, 4.57; N, 4.38. C$_{34}$H$_{28}$O$_4$N$_2$Ru. Calculated (%): C, 64.86; H, 4.45; N, 4.45. The ^{1}H NMR spectrum of complex **2b** contains a double set of signals for the protons in two nonequivalent six-membered azaoxaruthenacycles. Complex **2b**: ^{1}H NMR (CDCl$_3$), δ: 2.33, 2.40 (both s, 3 H each, Me); 5.68 (d, 1 H, J = 7.5 Hz); 5.88 (s, 1 H); 7.34 (d, 1 H, J = 7.5 Hz); 7.48 (s, 1 H); 6.69 (d, 2 H, C$_6\underline{H}_4$Me, J = 7.3 Hz); 6.90 (d, 2 H, C$_6\underline{H}_4$Me, J = 7.6 Hz); 7.63 (d, 2 H, J = 7.3 Hz); 7.90 (d, 2 H, C$_6$H$_4$Me, J = 7.6 Hz); 7.23—7.25 (m, 10 H, 2 Ph). The presence of two singlets at δ 5.88 and 7.48 instead of two expected doublets is probably due to the spatial arrangement of these protons.

Complex **2c**, decomp. 200 °C. Found (%): C, 64.71; H, 4.41; N, 4.35. C$_{34}$H$_{28}$O$_4$N$_2$Ru. Calculated (%): C, 64.86; H, 4.45; N, 4.45. Both chelate rings in complex **2c** have a different spatial orientation from that in **2a**, and corresponding changes appear in its IR and ^{1}H NMR spectra. The IR spectrum of complex **2c** exhibits two intense CO absorption bands characteristic of a *cis*-M(CO)$_2$ group (heptane, ν(CO)/cm^{-1}: 2034 vs, 1970 sh, 1960 vs). The ^{1}H NMR spectrum of complex **2c** contains a double set of signals for the protons of two six-membered azaoxaruthenacycles, which are nonequivalent because of close spatial vicinity of two Ph groups. Complex **2c**: ^{1}H NMR (CDCl$_3$), δ: 2.31, 2.33

(both s, 3 H each, Me); 5.70 (d, 1 H, J = 6.5 Hz); 6.55, 7.74 (both s, 1 H each); 7.08—7.67 (m, 19 H, 2 Ph, 2 C_6H_4Me, 1 H).

Interestingly, this reaction does not yield two possible isomers with *trans*-arrangement of the CO groups, probably because of a significant *trans*-effect of these ligands.

Hence, it was discovered that the reaction of 4-amino-1-oxabuta-1,3-diene **1** with $Ru_3(CO)_{12}$ affords three isomeric *cis*-dicarbonyl ruthenium(II) complexes each containing two six-membered azaoxaruthenacycles.

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