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$L' = CO$ vs Cl^- Transposition: Remarkable Consequences for the Product of $(L')-Ru(L)_2-(H)$ and Vinyl Ether

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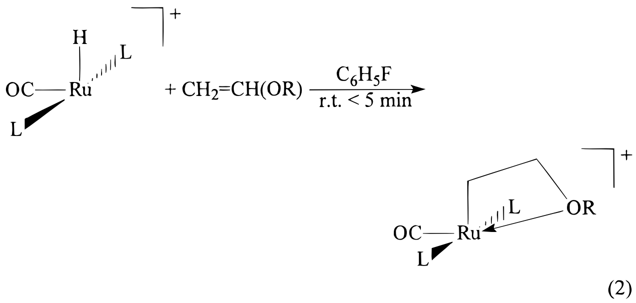
Summary: The products of reaction of $H_2C{=}CH(OR)$ with $RuH(Cl)L_2$ ($L = P^iPr_3$) and $RuH(CO)L_2^+$ ($L = P^tBu_2Me$) are $RuH(Cl)({=}C(OR)Me)L_2$ and $Ru(CO)(CH_2CH_2OR)L_2^+$, respectively. Spectroscopic data and X-ray analysis ($R = Me$, $B[C_6H_3(CF_3)_2]_4$ salt, hemi(pentane) solvate) reveal the presence, in the latter, of a β-alkoxy ethyl ligand with a Ru−O bond. DFT (B3PW91) calculations show that the observed products correspond to the thermodynamic preference.

We have reported earlier that the fragment $RuHClL_2$ ($L = P(^iPr)_3$), which exists as a dimer in noncoordinating solvents, isomerizes vinyl ethers to coordinated carbenes **A** (eq 1).[1] This is enabled kinetically[2] by the hydride

$$RuHClL_2 + H_2C{=}CH(OMe) \rightarrow L_2ClHRu(H_2C{=}CH(OMe)) \rightarrow \underset{\textbf{A}}{L_2ClHRu{=}CMe(OMe)} \quad (1)$$

ligand (eq 1), and the carbene is calculated to be isoenergetic with the π-olefin complex (an *observed* intermediate) due to the π-basicity of Ru(II) in this ligand environment;[3] that is, the π-acidic carbene benefits from back-donation by the $RuHClL_2$ substructure.[1] We now report experimental observations showing that replacement of Cl^- by CO leads to an isomeric product (eq 2), together with computational studies that help explain the newly observed product.

Addition of $CH_2{=}CH(OCH_3)$(excess) to $[RuH(CO)(P^tBu_2Me)_2]BAr'_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) in fluorobenzene (20 °C, <5 min) causes an immediate color change from light orange to bright orange. When the solution is layered with pentane at −20 °C for 2 days, large orange crystals are isolated in almost quantitative yield. NMR spectral data reveal clean formation of $[Ru(\eta^2\text{-}CH^a{}_2CH^b{}_2OCH^c{}_3)(CO)(P^tBu_2Me)_2]^+$ (**1**).[4] The ^1H NMR spectrum of **1** has an apparent quintet at 2.07 ppm ($J_{HH} = J_{PH} = 7.7$ Hz) for H^a and a triplet at 4.09 ppm (H^b) and a singlet at 3.04 ppm for H^c. Correspondingly, the $^{13}C\{^1H\}$ NMR spectrum gives singlets at 89.6 (CH_2O) and 60.6 ppm (OCH_3) and a triplet at −1.18 ppm ($J_{PC} = 5.5$ Hz) for $Ru-CH_2$. These data do not provide evidence for or against ether oxygen coordination. However, the CO stretching frequency (1939 cm^{-1}) of **1** is significantly lower than that of $[Ru(CH_3)(CO)L_2]^+$ (1951 cm^{-1}), consistent with ether oxygen coordination in **1** (eq 2). Vinyl ethyl ether reacts similarly to give **2**, although sterically more demanding vinyl *tert*-butyl ether does not react.



(2)

1. $R = CH_3$
2. $R = C_2H_5$

$L = P^tBu_2Me$

A crystal structure determination[5] (Figure 1) confirms what is deduced from the spectroscopic study: the vinyl ligand has inserted into the hydride−Ru bond, and the resulting β-methoxy ethyl ligand binds in an η^2 fashion

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(4) **$[Ru(\eta^2\text{-}CH_2CH_2OCH_3)(CO)(P^tBu_2Me)_2]BAr'_4$.** $[RuH(CO)L_2]BAr'_4$ (200 mg, 152 mmol) was dissolved in C_6H_5F (5 mL); an excess of methyl vinyl ether was vacuum-transferred into this solution, and the mixture was stirred for 5 min. The volatiles were evaporated, and the residue was recrystallized in C_6H_5F layered with pentane. Yield: 190 mg (92%). ^1H NMR ($C_6H_5F:C_6D_{12} = 10:1$, 20 °C, 400 MHz): δ 4.09 (t, $J_{HH} = 7.7$ Hz, 2H, CH_2O), 3.04 (s, 3H, OCH_3), 2.07 (tt, $J_{HH} = 7.7 = J_{PH} = 7.7$ Hz, $Ru-CH_2$), 1.13 (vt, $N = 13.7$ Hz, 18H, $PC(CH_3)_3$), 1.09 (vt, $N = 5.0$ Hz, 6H, PCH_3), 0.90 (vt, $N = 13.0$ Hz, 18H, $PC(CH_3)_3$). $^{31}P\{^1H\}$ NMR (162 MHz): δ 45.0 (s). $^{13}C\{^1H\}$ NMR (100 MHz): δ 205.4 (t, $J_{PC} = 15$ Hz, Ru−CO), 89.6 (s, CH_2O), 60.6 (s, OCH_3), 38.0 (vt, $N = 18$ Hz, $P\mathit{C}(CH_3)_3$), 36.6 (vt, $N = 18$ $P\mathit{C}(CH_3)_3$), 29.3 and 29.0 (s, $PC(\mathit{C}H_3)_3$), 2.9 (vt, $N = 17.4$ Hz, PCH_3), −1.18 (t, $J_{PC} = 5.5$ Hz). IR (C_6H_5F): 1939 cm^{-1} (ν(CO)). Elemental analyses, which will differ insignificantly from the reagent complex, were not obtained.

(5) Crystal data (−174 °C) for $C_{57}H_{61}BF_{24}O_2P_2Ru$ (which is the salt together with 0.5 molecule of pentane, disordered by a C_2 axis): $a = 13.622(2)$ Å, $c = 34.616(3)$ Å, with $Z = 4$ in space group $P4_12_12$. $R(F) = 0.0663$ and $R_w(F^2) = 0.1574$ for 3819 observed ($F > 4\sigma(F)$) data out of 5679 unique intensities measured. The cation is disordered around a C_2 axis, and restraints are required to obtain a satisfactory refinement. Structural parameters are thus to be interpreted with great caution.

10.1021/om990649g CCC: $18.00

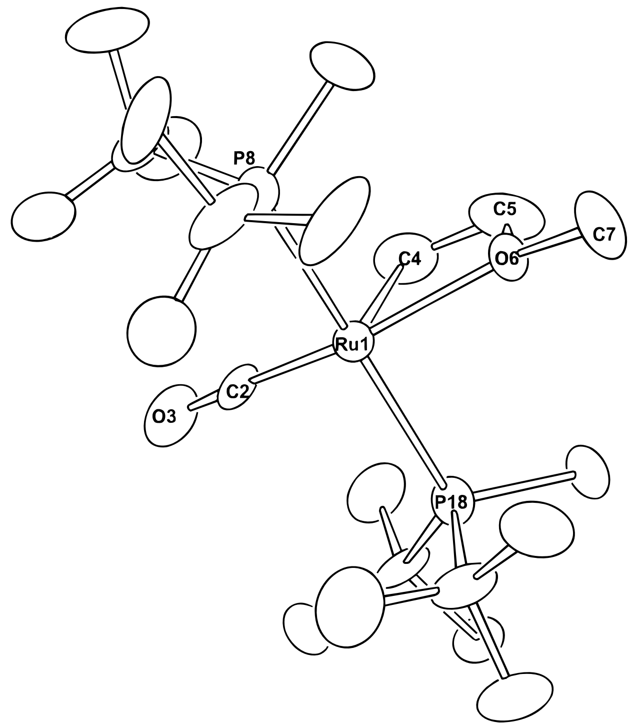

Figure 1. ORTEP drawing (30% probability ellipsoids) of the non-hydrogen atoms of $Ru(\eta^2\text{-}CH_2CH_2OMe)(CO)(P^tBu_2\text{-}Me)_2^+$. Unlabeled atoms are phosphine substituent carbons. Ru−C1 = 1.796(15) Å, Ru−C2 = 2.068(13) Å; C1−Ru−C2 = 94.0(7)°, C2−Ru−O2 = 63.2(14)°.

through an alkyl carbon and the methoxy oxygen. The Ru−O distance is 2.226(8) Å.

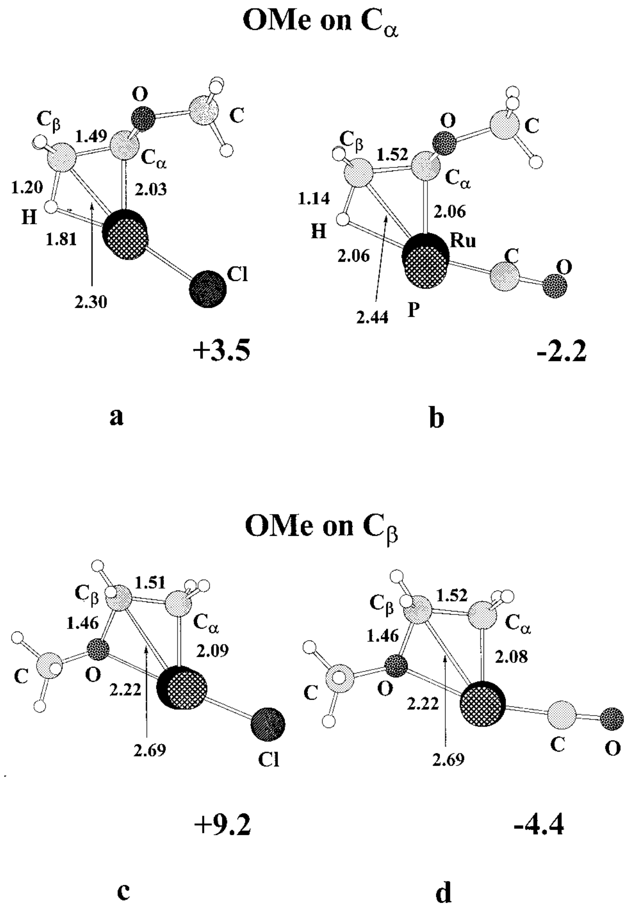

Figure 2. DFT(B3PW91) optimized structure for the most favorable alkyl complexes: (top) $RuL'(PH_3)_2(CH(OMe)\text{-}(CH_3))$; (bottom) $RuL'(PH_3)_2(CH_2CH_2OMe)$. Energies are given in kcal/mol, relative to the vinyl methyl ether adduct, and distances are given in Å.

The DFT(B3PW91) calculations[6−12] show that the significant binding energy of the π-olefin adduct to $RuHL'(PH_3)_2$ is remarkably insensitive to the nature of L′, since they differ by less than 3 kcal/mol (Cl^-, 35.7 kcal/mol; CO, 33.1 kcal/mol). The relative energy of the carbene and the π-olefin adduct is also insensitive to the nature of L′. The most stable carbene complexes are 1.6 kcal/mol ($L' = Cl^-$) or 2.2 kcal/mol ($L' = CO$) above the most stable π-olefin adduct. Therefore, replacing Cl^- by CO does not change in any significant manner the thermodynamics of the transformation of the vinyl ether into alkoxycarbene complexes. In contrast, the energy and structure of the alkyl isomers (Figure 2) resulting from the insertion of the C=C bond in the Ru−H bond in the two possible orientations depend significantly on L′. With $L' = Cl^-$, the π-olefin adduct (used as reference for energy) is *below* the most stable alkyl isomer (OMe on the α-carbon and β-C−H agostic bond: **a**, +3.5 kcal/mol) and *below* isomer **c** (OMe on the β-carbon; +9.2 kcal/mol). With L′ = CO, the π-olefin adduct is *above* the most stable alkyl isomer (OMe on the β-carbon: **d**, −4.4 kcal/mol) and isomer **b** (−2.2 kcal/mol). Thus, the primary consequence of the replacement of Cl^- by CO is to stabilize the alkyl isomers regardless of the direction of insertion of the C=C bond into the Ru−H bond. This leads to an alkyl complex which can effectively compete with the isomeric olefin or carbene adducts. The structure of **d** compares very well with the experimental structure (Figure 1).

To assess the role of L′ in lowering the energy of isomer **d**, alkyl rotamers (**e** for $L' = Cl^-$ and **f** for L′ = CO) deprived of any Ru···O or C−H agostic interactions were considered as true 14-electron complexes.[13] The alkyl isomers **e** and **f** are 24.2 and 19.3 kcal/mol above the corresponding π-olefin adduct. This shows that the

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[6] The calculations were carried out with the Gaussian 98 suite of programs: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.6; Gaussian, Inc., Pittsburgh, PA, 1998. Ru was represented with the Hay−Wadt relativistic core potential (ECP) for the 28 innermost electrons and its associated double-ζ basis set.[7] Cl and P are also described with the Los Alamos ECPs and their associated double-ζ basis set augmented by a d polarization function.[8,9] A 6-31G(d,p) basis set[10] was used for all other atoms. Full optimizations without symmetry constraint have been carried out at the B3PW91 level.[11,12]

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[13] The alkyl chain is constrained to have eclipsed α-C−H and Ru−L′ bonds, which puts the two other CH_3 and OMe substituents away from the empty sites of Ru.

alkyl complex is intrinsically more energetically accessible for L′ = CO than for L′ = Cl^-. While they have essentially identical geometrical features, cleaving the Ru−O bond (going from **c** to **e** for L′ = Cl^- and from **d** to **f** for L′ = CO) to give a 14-electron complex costs 15.0 kcal/mol for L = Cl^- but 23.7 kcal/mol for L′ = CO. This significant difference in Ru−O binding energy could be due to orbital interactions involving the π-donor or -acceptor L′ ligand and/or to electrostatic factors. The factors that control the role of L′ on the relative energies of the alkyl, carbene, and olefin isomers are under study.

This result is another example where replacement of Cl^- by CO induces ligand coupling instead of metal−ligand bond formation. This principle thus has some generality.[14]

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Supporting Information Available: Tables giving crystallographic details, positional and thermal parameters, and bond distances and angles and figures giving NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org..

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