Journal of Organometallic Chemistry, 174 (1979) C11—C14

Preliminary communication

SYNTHESIS AND X-RAY STRUCTURE OF CHLOROCARBONYL N-ISOPROPENYL-N'-ISOPROPYLFORMAMIDINATOBIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)-FACILE DEHYDROGENATION OF A COORDINATED ISOPROPYL GROUP.

By Arlo D. Harris, Stephen D. Robinson* and Arvind Sahajpal

(Department of Chemistry, King's College, Strand, London WC2R 2LS.)

and Michael B. Hursthouse.*

(Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS.)

(Received May 8th, 1979)

Summary. The title compound, prepared by heating [RuHCl(CO)(PPh$_3$)$_3$] with di-isopropylcarbodiimide (Pr^{i}N=C=NPr^i) in boiling benzene, has been shown by ^{1}H n.m.r. and X-ray diffraction methods to contain the N-isopropenyl-N'-isopropylformamidinate ligand generated by insertion of the carbodiimide moiety into the Ru-H bond and the concomitant loss of molecular hydrogen from one of the isopropyl groups.

We have previously reported the synthesis of N,N'-diarylformamidinato complexes of some platinum group metals by insertion of N,N'-diarylcarbodiimides into metal-hydride linkages [1,2]. In contrast to diarylcarbodiimides, the corresponding dialkyl compounds, as exemplified by di-isopropylcarbodiimide, are reluctant to react with platinum metal hydrides. However, in refluxing benzene di-isopropylcarbodiimide and the complexes [RuHX(CO)(PPh$_3$)$_3$] (X = Cl or Br) generate new products of stoichiometry [RuX(C$_7$H$_{13}$N$_2$)(CO)(PPh$_3$)$_2$] in ca 85% yield as air-stable yellow crystals. The ^{1}H n.m.r. spectra of the

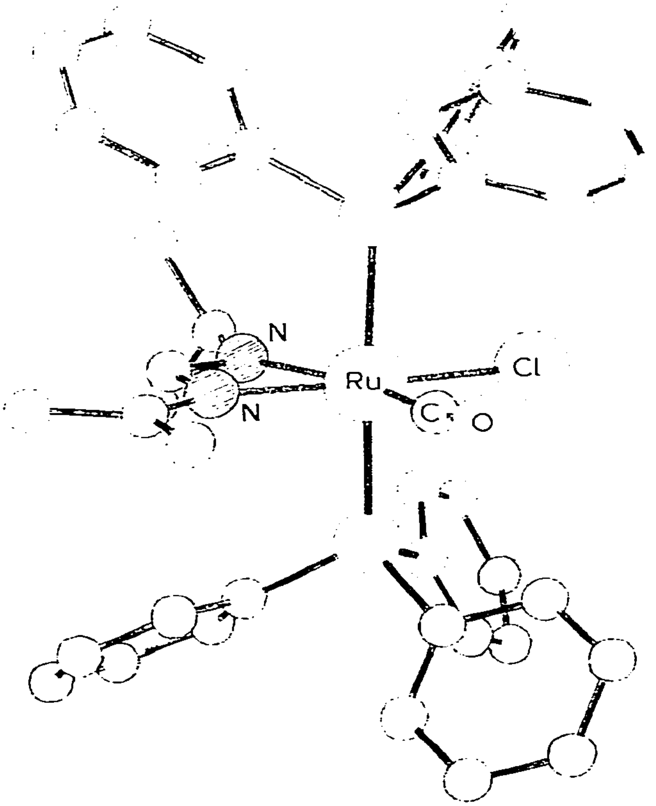

Figure: A molecule of chlorocarbonyl N-isopropenyl-N'-isopropylformamidinatobis(triphenylphosphine)ruthenium(II). Some significant bond lengths are: Ru-N 2.05(1), Ru-N' 2.23(1), Ru-Cl 2.432(3), Ru-C 1.81(1), Ru-P 2.383(3), 2.400(3) Å.

new complexes are consistent with the presence of an N-isopropenyl-N'-isopropylformamidinate ligand [X = Cl; $-C(Me)=CH_2$ group, τ_{Me} 9.30(s), τ_{CH_2} 6.43(s) and 6.81(s); $-CH(Me)_2$ group τ_{Me} 9.34(d), τ_{CH} 6.15 (septet), $^3J(HH')$ 6.5 Hz] and, this has been confirmed by a single crystal X-ray diffraction study of the complex $[RuCl(C_7H_{13}N_2)(CO)(PPh_3)_2]$.

Crystal data: Monoclinic, space group $P2_1/a$ with $\underline{a}$ = 17.836(2), $\underline{b}$ = 18.443(3), $\underline{c}$ = 12.607(1) Å, β = 104.59°, Z = 4. Intensities of 6412 reflections were measured on a Nonius CAD4 diffractometer using Ni-filtered Cu-K_α radiation;

of these 4381 were deemed observed. The structure was solved and refined by standard methods, and the current R value is 0.086.

The molecular structure is shown in the Figure. The phosphines have a mutual *trans* configuration and the chlorine atom is *trans* to the nitrogen atom of the formamidinate ligand to which the N-*iso*propenyl group is attached. The two Ru-N distances are significantly different with that *trans* to chlorine the shorter of the two. This feature may result from the greater *trans* influence of the carbonyl ligand. The exocyclic double bond is not bound to the metal atom (closest approach 3.27Å) but is held approximately co-planar with the chelate ring and is apparently conjugated with the π-electron system of the latter. Presumably formation of this conjugated system is one factor favouring occurrence of the dehydrogenation reaction. Transition metal mediated reactions involving cleavage of carbon-hydrogen bonds are common [3], however dehydrogenation of alkyl groups to form non-coordinated double bonds is relatively rare. Recently examples involving dehydrogenation of cyclohexyl groups in coordinated tricyclohexylphosphine have been reported [4,5]. However, to our knowledge the present work affords the first example of transition metal mediated dehydrogenation of an alkyl group under mild conditions leading to formation of an exocyclic double bond. Attempts to prepare other complexes containing the N-*iso*propenyl-N'-*iso*propylformamidinate ligand have met little success; many platinum metal hydrides including $[RuH_2(CO)(PPh_3)_3]$ and $[OsHCl(CO)(PPh_3)_3]$ failed to react with di*iso*propylcarbodiimide. However, $[OsH_2(CO)(PPh_3)_3]$ does afford as the major product the formamidinato complex $[OsH(Pr^iN\underline{\cdots}CH\underline{\cdots}NPr^i)(CO)(PPh_3)_2]$ which, on further heating (6 h. boiling toluene), is quantitatively converted into the dehydrogenated species $[OsH\{Pr^iN\underline{\cdots}CH\underline{\cdots}NC(Me)=CH_2\}(CO)(PPh_3)_2]$. Attempts to observe other examples of *iso*propyl group dehydrogenation and to elucidate the mechanism of the dehydrogenation process are in progress.

We thank the SRC for financial support, and one of us (ADH) thanks California State College, San Bernardino for sabbatical research leave.

1. S.D. Robinson and A. Sahajpal, J. Organometallic Chem., 1976, 117, C111.
2. L.D. Brown, S.D. Robinson, A. Sahajpal and J.A. Ibers, Inorg. Chem., 1977, 16, 2728.
3. G.W. Parshall, Catalysis (London) 1977, 1, 335 and references therein.
4. S. Hietkamp, D.J. Stufkens and K. Vrieze, J. Organometallic Chem., 1978, 152, 347.
5. B.R. James, M. Preece and S.D. Robinson, Inorg. Chim. Acta, submitted for publication.