Journal of Organometallic Chemistry, 236 (1982) C61—C64
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE FORMATION AND INTRAMOLECULAR REACTIONS OF SOME μ-ALKYLIDENE COMPLEXES, $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)\{\mu(\eta^1\text{-}CF_3C_2CF_3)$

RON S. DICKSON*, GARY D. FALLON, RHONDA J. NESBIT, and GEOFF N. PAIN
Department of Chemistry, Monash University, Clayton, Victoria 3168 (Australia)

(Received June 20th, 1982)

Summary

Treatment of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu(\eta^2\text{-}CF_3C_2CF_3)\}$ with diazo compounds $N_2CR^1R^2$ gives the μ-alkylidene complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)\{\mu(\eta^1\text{-}CF_3C_2CF_3)\}$ (I, $R^1 = R^2 = H$; II, $R^1 = H$, $R^2 = CF_3$; III, $R^1 = H$, $R^2 = CO_2Et$; IV, $R^1 = R^2 = CO_2Et$). In solution, I and III are converted to $(\eta\text{-}C_5H_5)_2Rh_2\{\mu(\eta^1,\eta^3\text{-}C(CF_3)C(CF_3)CHR^2)\}$ by insertion of the alkylidene unit into an alkyne—rhodium bond. This reaction is not observed for II. With IV, a related insertion reaction produces $(\eta\text{-}C_5H_5)_2Rh_2\{C(CF_3)\text{=}C(CF_3)OC(OEt)\text{=}C(CO_2Et)\}$. The crystal and molecular structure of this complex has been determined from single crystal X-ray diffraction data.

The recent literature contains several accounts of the formation, structures, and reactions of μ-alkylidenedimetal complexes [1, 2]. The considerable interest in these compounds is due to their probable involvement in important transition metal-catalyzed processes such as olefin metathesis and Fischer—Tropsch chemistry. In our investigations of some μ-alkylidenedirhodium complexes, we have established that the substituents on the alkylidene-carbon have a significant influence on intramolecular reactions that occur between the alkylidene and another ligand that is also attached to the Rh_2 centre. In this communication, we outline this substituent effect.

A range of μ-alkylidene complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)\{\mu(\eta^1\text{-}CF_3\text{-}C_2CF_3)\}$ is obtained by treating $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu(\eta^2\text{-}CF_3C_2CF_3)\}$ with various diazoalkanes $N_2CR^1R^2$ (e.g. $R^1 = R^2 = H$; $R^1 = H$, $R^2 = CF_3$ or CO_2Et; $R^1 = R^2 = CO_2Et$). The reactions are performed in diethyl ether at 0°C; a rapid colour change from green to orange-red is observed, and crystals of complexes I—IV are deposited upon evaporation of the solvent. Yields of the complexes

---

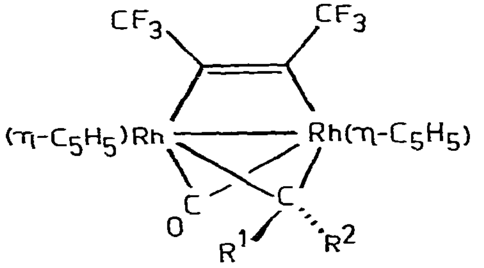
*To whom correspondence should be sent.

0022-328X/82/0000—0000/$02.75

are high (e.g. 85% for I). Each of the complexes has been obtained analytically pure, and is characterized from spectroscopic data (e.g. I, R^1 = H, R^2 = H; IR ($CHCl_3$ soln.) ν(CO) at 1875 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 10.55 ppm (dt, 1H, CH^1H^2, J(HH) 5, J(RhH) 2.5 Hz), 7.84 ppm (dt, 1H, CH^1H^2, J(HH) 5, J(RhH) 1 Hz), 5.65 ppm (s, 10H, C_5H_5); ^{19}F NMR ($CDCl_3$) δ 53.2(s) ppm).

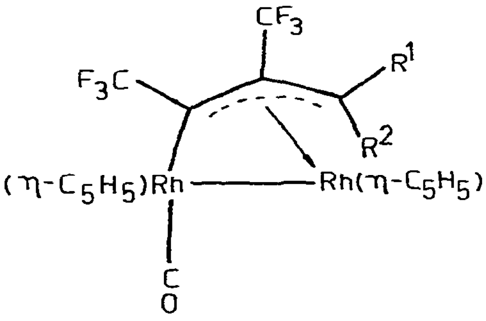
When solutions of I in chlorinated hydrocarbons are kept at room temperature for some time, a new product can be isolated by thin layer chromatography. The spectroscopic properties of this compound (IR (KBr), ν(CO) at 2005, 1995 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 5.39 (d, 5H, C_5H_5), 5.29 (d, 5H, C_5H_5), 3.41 (m, 1H, CH), 2.46 ppm (m, 1H, CH); ^{19}F NMR ($CDCl_3$) δ 46.5, 57.4 ppm (2 x q, J(FF) 13 Hz) are consistent with structure V in which the methylene fragment has inserted into an alkyne—rhodium bond. The proposed structure is similar to that established for $(\eta\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)(CO)\{MeO_2CC_2CO_2\text{-}MeCHMe\}$ by single crystal X-ray diffraction [3].

Solutions of II in $CHCl_3$ or CH_2Cl_2 remain unchanged after several days at room temperature. There is no conversion to V (R^1 = H, R^2 = CF_3), even when the solutions are refluxed for several hours. There is, however, ready formation of V (R^1 = H, R^2 = CO_2Et) from III in $CHCl_3$ at room temperature, and this reaction has been monitored by ^1H and ^{19}F NMR spectroscopy. An interesting feature of this conversion is the involvement of isomers of both III and V in the insertion reaction. These isomers arise from different orientations of the substituents R^1 and R^2. At room temperature (or more quickly in refluxing solvents), a solution of IIIa (δ (CH) at 7.50 ppm) is converted to a mixture of IIIa, IIIb (δ (CH) at 10.49 ppm), Va (δ (CH) at 3.4 ppm), and Vb (δ (CH) at 4.10 ppm) (see Table 1). Pure Va could be obtained by repeated TLC of the reaction mixture, but Vb could not be isolated free from Va.

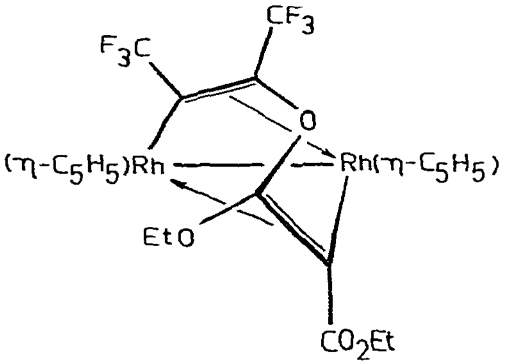


(I, R^1 = R^2 = H ;
II, R^1 = H, R^2 = CF_3 ;
III, R^1 = H, R^2 = CO_2Et ;
IV, R^1 = R^2 = CO_2Et)

Formation of the complex IV is followed by an intramolecular reaction in solution to produce VI. The structure of this complex could not be deduced unambiguously from spectroscopic data, and consequently a single crystal X-ray study was undertaken.



(V)



(VI)

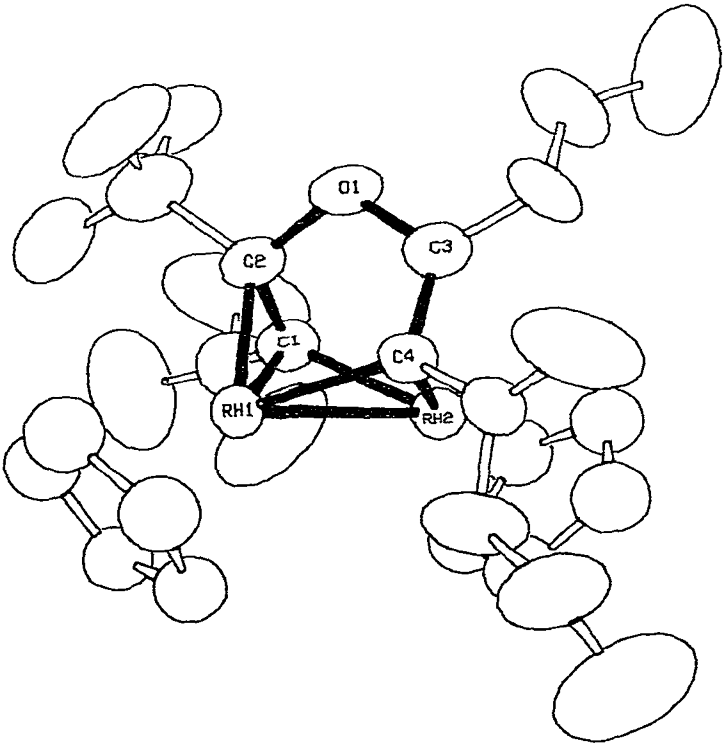


Fig. 1. Molecular structure of $(\eta\text{-}C_5H_5)_2Rh_2\{C(CF_3)C(CF_3)OC(OEt)C(CO_2Et)\}$. Bond lengths: Rh(1)—Rh(2) 2.609(1), Rh(1)—C(1) 2.097(10), Rh(1)—C(2) 2.095(9), Rh(1)—C(4) 2.022(8), Rh(2)—C(1) 2.024(9), Rh(2)—C(4) 2.074(8), C(1)—C(2) 1.438(12), C(2)—O 1.425(10), O—C(3) 1.338(10), C(3)—C(4) 1.440(12) A°.

Crystal data: $C_{21}H_{20}F_6O_4Rh_2$, $M = 656.2$, monoclinic, a 17.666(8), b 13.679(6), c 9.526(4) Å, β 103.62(8)°, D_m 1.90(3) g cm^{-3}, D_c 1.95 g cm^{-3}, $Z = 4$, space group $P2_1/n$, $F(000) = 1288$.

Single crystal X-ray diffraction data, between the limits $6° < \theta < 30°$, were measured with a Philips PW 1100 X-ray diffractometer using a ω-scan tech-

TABLE 1

THE EFFECTS OF TIME AND TEMPERATURE ON THE CONVERSION OF III TO V, $R' = H$, $R^2 = CO_2Et$.

Conditions	Relative amounts (%) of species			
	IIIa	IIIb	Va	Vb
25°C, 24 h	50	40	10	—
35°C, 48 h	—	50	40	10
reflux, 1—2 min	<5	15	70	10
reflux, 20 min	—	<10	50	40

nique with graphite monochromated Mo-K_α radiation. For 2945 unique reflections $[I \geqslant 3\sigma(I)]$ R is 0.052*. A representation of the molecular structure, and some selected bond parameters, are given in Fig. 1. The formation of VI from IV involves insertion of a carboxylic oxygen (rather than the alkylidene carbon) into the alkyne—rhodium bond. π-Coordination of each alkene function in the bridging unit, $C(CF_3)=C(CF_3)OC(OEt)=C(CO_2Et)$, results in displacement of the carbonyl ligand from IV.

The reactions studied establish that the μ-alkylidene unit is highly reactive towards a coordinated alkyne (but not coordinated CO) in these Rh_2 complexes. Depending on the substituents attached to the alkylidene, formation of new C—C and C—O bonds can occur under mild conditions. The study of these systems is currently being extended in our laboratory.

Acknowledgement. This work was supported by a grant from the Australian Research Grants Scheme.

References

1 W.A. Herrmann, Adv. Organometal. Chem., and ref. therein, in press.
2 (a) A.F. Dyke, S.A.R. Knox, K.A. Mead, and P. Woodward, Chem. Commun., (1981) 861; (b) J. Levisalles, F. Rose-Munch, H. Rudler, J.-C. Daran, Y. Dromzee, and Y. Jeannin, Chem. Commun., (1981) 152; (c) K. Isobe, D.G. Andrews, B.E. Mann, and P.M. Maitlis, Chem. Commun., (1981) 809; (d) M. Cooke, D.L. Davies, J.E. Guerchais, S.A.R. Knox, K.A. Mead, J. Roué, and P. Woodward, Chem. Commun., (1981) 862; (e) K.H. Theopold and R.G. Bergman, J. Amer. Chem. Soc., 103 (1981) 2489; (f) B.B. Meyer, P.E. Riley, and R.E. Davis, Inorg. Chem., 20 (1981) 3024; (g) F. Takusagawa, A. Fumagalli, T. Koetzle, and W.A. Herrmann, Inorg. Chem., 20 (1981) 3060; (h) P.A. Dimas and J.R. Shapley, J. Organometal. Chem., 228 (1982) C12; (i) W.A. Herrmann and C. Bauer, Chem. Ber., 115 (1982) 14; (j) C.P. Casey, P.J. Fagan, and W.H. Miles, J. Amer. Chem. Soc., 104 (1982) 1134; (k) W.A. Herrmann and C. Bauer, Chem. Ber., 115 (1982) 14; (l) W.A. Herrmann and J.M. Huggins, Chem. Ber., 115 (1982) 396; (m) J. Müller, B. Passon, and J. Pickardt, J. Organometal. Chem., 228 (1982) C51.
3 A.F. Dyke, S.A.R. Knox, P.J. Naish, and G.E. Taylor, Chem. Commun., (1980) 803.

---

* Atomic coordinates for this work are available from the author.