

### Preliminary communication

## REACTION OF THE UNSATURATED COMPLEX $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CO})]_2$ WITH DIAZO COMPOUNDS

ALLEN D. CLAUSS, PETER A. DIMAS and JOHN R. SHAPLEY\*

*Department of Chemistry, University of Illinois, Urbana, Illinois 61801 (U.S.A.)*

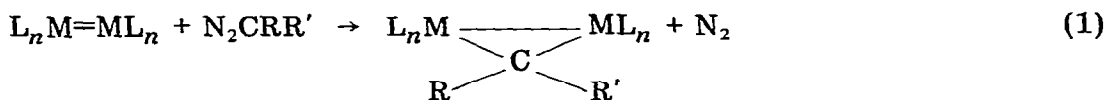
(Received August 8th, 1980)

### Summary

The compounds  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CRR}')$  ( $\text{R} = \text{H}$ ;  $\text{R}' = \text{H}, \text{Me}, \text{CO}_2\text{Et}$ ;  $\text{R} = \text{R}' = \text{Ph}$ ) have been synthesized by direct reaction of the corresponding diazo reagents  $\text{N}_2\text{CRR}'$  with the unsaturated dirhodium compound  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CO})]_2$ . Sublimation of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CPh}_2)$  results in decarbonylation to give the unsaturated dirhodium compound  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]_2(\mu\text{-CO})(\mu\text{-CPh}_2)$ .

Diazo compounds are common reagents for the preparation of transition metal  $\mu$ -alkylidene complexes [1a]. Dimeric  $\mu$ -alkylidene complexes of manganese, cobalt, and rhodium have been isolated from the reactions of diazo compounds with monomeric complexes of these metals. [1b–1f]\*. However, the most direct path for formation of such cyclic compounds (eq. 1) in analogy with organic reactions, namely, the direct reaction of a diazo compound with a complex containing a metal–metal double bond has not been demonstrated. Diazomethane reacts with the unsaturated cluster  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  to yield an equilibrium mixture of hydrido- $\mu$ -methyl- and dihydrido- $\mu$ -methylene-triosmium clusters; however, the initial step of this reaction is formation of the  $\mu$ -methyl compound by insertion of methylene into an Os–H bond [2]. Direct insertion of a carbene into a metal–metal single bond is observed in the reaction of diazomethane with  $\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2$  (dppm = bis(diphenylphosphino)methane) which results in the formation of a  $\mu$ -methylene compound with no metal–metal bond [3]. We wish to report here the first examples demonstrating eq. 1.

\* $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}]_2(\mu\text{-CO})(\mu\text{-CPh}_2)_2$  was prepared by treating  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  with  $\text{Ph}_2\text{CN}_2$  followed by  $\text{NaC}_5\text{H}_5$ . Heating the product in solution resulted in the formation of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}]_2(\mu\text{-CPh}_2)_2$  [1f].



Treatment of deep blue dichloromethane solutions of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CO})]_2$  [4] with excess diazomethane, diazoethane, ethyldiazoacetate or diphenyldiazomethane at room temperature resulted in a rapid color change to dark red. In the case of diazomethane the methylene chloride was removed in vacuo and the residue was extracted with pentane. Evaporation of the pentane extract yielded  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CH}_2)$ , a dark red solid, as the only observed product. The compound was further purified by sublimation ( $80^\circ\text{C}$ ,  $10^{-1}$  torr, 51% yield). The red solution resulting from reaction with diazoethane was taken to dryness and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CHCH}_3)$  was sublimed ( $80^\circ\text{C}$ ,  $10^{-2}$  torr) from the residue (52% yield). Similar work-up of the ethyl-diazoacetate reaction afforded a red oil after sublimation. Recrystallization of the red oil from petroleum ether at  $-78^\circ\text{C}$  yielded  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CHCO}_2\text{Et})$  as a red powder (5%). The reaction with diphenyldiazomethane proceeded similarly to yield  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CPh}_2)$  as a red solid (64% yield); attempted purification of this compound by sublimation (0.1 torr,  $130^\circ\text{C}$ ) resulted in decarbonylation to give the dark green unsaturated complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]_2(\mu\text{-CO})(\mu\text{-CPh}_2)$ .

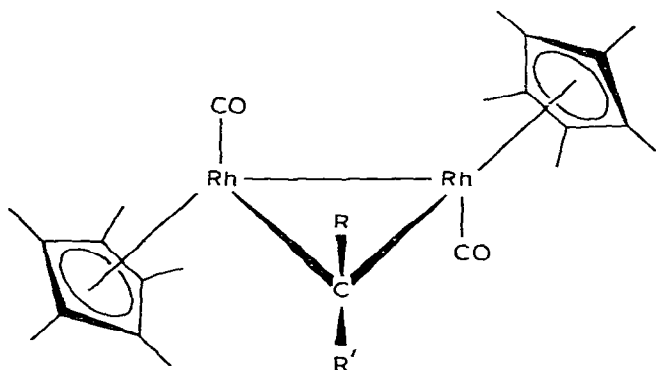
The IR,  $^1\text{H}$  NMR (Table 1) and mass spectroscopic data for these compounds confirm their formulation as  $\mu$ -alkylidene derivatives. The mass spectrum of each compound shows a strong molecular ion peak as well as peaks for the expected fragment ions. The compounds  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CHR})$  ( $R = \text{H, Me, CO}_2\text{Et}$ ) exhibit a strong terminal  $\nu(\text{CO})$  band in the IR spectrum and a low field resonance in the  $^1\text{H}$  NMR due to the hydrogen atom(s) bound to the alkylidene carbon. These spectral characteristics are in close agreement with those of the previously characterized compounds  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CHR})$  ( $R = \text{H, Me, CO}_2\text{Et}$ ) suggesting analogous struc-

TABLE 1

IR AND  $^1\text{H}$  NMR DATA FOR  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CRR}')$  AND  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]_2(\mu\text{-CO})(\mu\text{-CPh}_2)$ 

Compound	IR ( $\text{cm}^{-1}$ )	$^1\text{H}$ NMR ( $\tau$ , $\text{CDCl}_3$ )
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CH}_2)$	1946(s) <sup>a</sup>	4.05 (s, 2H) 8.03 (s, 30 H)
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CHCH}_3)$	1934(s) <sup>b</sup>	2.96 (q, 1H) 7.77 (d, 3H, $J$ 6.8 Hz) 8.09 (s, 30H)
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CHCO}_2\text{Et})$	1961(s) <sup>b</sup>	4.22 (m, 1H) 5.97 (q, 2H) 8.07 (s, 30H) 8.83 (t, 3H, $J$ 7.5 Hz)
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CPh}_2)$	1947(s) <sup>a</sup>	
$[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]_2(\mu\text{-CO})(\mu\text{-CPh}_2)$	1751(s) <sup>b</sup>	2.95 (m, 10H) 8.65 (s, 30H)

<sup>a</sup> Cyclohexane solution. <sup>b</sup> Dichloromethane solution.



(I)

tures (I) [1d]\*. However, in the pentamethylcyclopentadienyl compounds the alkylidene  $\alpha$ -hydrogen resonances are shifted upfield by 1.1 ppm ( $\mu$ -CH<sub>2</sub>), 1.6 ppm ( $\mu$ -CHCH<sub>3</sub>) and 1.5 ppm ( $\mu$ -CHCO<sub>2</sub>Et) whereas the carbonyl stretching frequencies are shifted to lower energy by 38 cm<sup>-1</sup> ( $\mu$ -CH<sub>2</sub>), 36 cm<sup>-1</sup> ( $\mu$ -CHCH<sub>3</sub>) and 23 cm<sup>-1</sup> ( $\mu$ -CHCO<sub>2</sub>Et) from those of the cyclopentadienyl derivatives [5]. This is in accord with the expected greater electron-donating ability of the C<sub>5</sub>Me<sub>5</sub> ligands. This attribute apparently also affects the physical properties, since, unlike the C<sub>5</sub>H<sub>5</sub> derivatives, the C<sub>5</sub>Me<sub>5</sub> compounds are moderately air sensitive and decompose instantly on silica gel.

In contrast to the monosubstituted methylene derivatives, the diphenylmethylene compound  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CPh}_2)$  readily decarbonylates (130°C, 0.1 torr) to yield  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]_2(\mu\text{-CO})(\mu\text{-CPh}_2)$ , an intensely colored green compound which presumably contains a rhodium-rhodium double bond. The compound exhibits a very low energy bridging carbonyl band in the IR and the C<sub>5</sub>Me<sub>5</sub> resonance in the <sup>1</sup>H NMR is shifted upfield from those of the dicarbonyl alkylidenes. These spectral features are also observed for the parent compound  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})]_2$  [4]. Other closely related unsaturated compounds containing  $\mu$ -alkylidene ligands have been reported [1e,6], but only in the case of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}]_2(\mu\text{-CPh}_2)_2$  was the product formed directly by decarbonylation of a saturated precursor [1f].

This work has been supported by a grant from The National Science Foundation and by fellowships from the A.P. Sloan Foundation and the Camille and Henry Dreyfus Foundation to J.R.S. The authors wish to thank Dr. T.J. Mazanec for helpful discussions and a generous gift of C<sub>5</sub>Me<sub>5</sub>Rh(CO)<sub>2</sub>.

\* $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CH}_2)$ : IR ( $\nu(\text{CO})$ , pentane) 1984(vs) <sup>1</sup>H NMR ( $\tau$ , acetone-*d*<sub>6</sub>) 2.93 (q, 1H);  
 $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CHMe})$ : IR ( $\nu(\text{CO})$ , pentane) 1970(vs) <sup>1</sup>H NMR ( $\tau$ , acetone-*d*<sub>6</sub>) 1.32 (m, 1H);  
 $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2(\mu\text{-CHCO}_2\text{Et})$ : IR ( $\nu(\text{CO})$ , CH<sub>2</sub>Cl<sub>2</sub>) 1984(s) <sup>1</sup>H NMR ( $\tau$ , CDCl<sub>3</sub>) 2.76 (m, 1H) [5].

## References

- 1 (a) For a recent review: W.A. Herrmann, *Angew. Chem. Int. Ed.*, **17** (1978) 800; (b)  $[(\eta^5\text{-RC}_5\text{H}_4)\text{-Mn}(\text{CO})_2]_2$ : W.A. Herrmann, B. Reiter and H. Biersack, *J. Organometal. Chem.*, **97** (1975) 245; (c)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})]_2(\mu\text{-CRCO}_2\text{R})$ : W.A. Herrmann, *Chem. Ber.*, **111** (1978) 1077; (d)  $[(\eta^5\text{-C}_5\text{H}_5)\text{-Rh}(\text{CO})]_2[\mu\text{-C}(\text{CO}_2\text{CH}_2\text{CH}_3)_2]$ : W.A. Herrmann, C. Kruger, R. Goddard and I. Bernal, *J. Organometal. Chem.*, **140** (1977) 73; (e)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_2(\mu\text{-CO})(\mu\text{-CPh}_2)$ : W.A. Herrmann and I. Schweiger, *Z. Naturforsch. B*, **33** (1978) 911; (f) T. Yamamoto, A.R. Garber, J.R. Wilkinson, C.B. Boss, W.E. Streib and L.J. Todd, *J. Chem. Soc., Chem. Commun.*, (1974) 354.
- 2 R.B. Calvert and J.R. Shapley, *J. Amer. Chem. Soc.*, **99** (1977) 5225.
- 3  $\text{Pt}_2\text{Cl}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2(\mu\text{-CH}_2)$ : M.P. Brown, J.R. Fisher, S.J. Franklin, R.J. Puddephatt and K.R. Seddon, *J. Chem. Soc., Chem. Commun.*, (1978) 749.
- 4 A. Nutton and P.M. Maitlis, *J. Organometal. Chem.*, **166** (1979) C21.
- 5 K.K. Mayer and W.A. Herrmann, *J. Organometal. Chem.*, **182** (1979) 361.
- 6 T.R. Halbert, M.E. Leonowicz and D.J. Maydonovitch, *J. Amer. Chem. Soc.*, **102** (1980) 5101.