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Preliminary communication

REACTION OF THE UNSATURATED COMPLEX $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]BF_4$ WITH DIAZO COMPOUNDS

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Summary

The unsaturated compound $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]BF_4$, prepared from $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ and $NOBF_4$, reacts with diazo reagents N_2CRR' to form, after decarbonylation, the unsaturated alkylidene compounds $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CRR')]BF_4$.

The direct reaction of diazo compounds with complexes containing a formal metal—metal double bond is a well established, general synthetic route to μ-alkylidene complexes [1]. The unsaturated rhodium dimer $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$ [2] reacts with diazo compounds in this manner to form complexes of the formula $[(\eta^5\text{-}C_5Me_5)Rh(CO)]_2(\mu\text{-}CRR')$. If the alkylidene ligand is large and resonance-stabilizing, e.g. $\mu\text{-}CPh_2$, the initial complexes may be decarbonylated to the unsaturated complexes $(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CRR')$. The recent report of the synthesis of $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]PR_6$ and related compounds [3] prompts us to communicate our findings concerning the reactions of the unsaturated complex $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]BF_4$ with diazo compounds to form, after decarbonylation, a series of unsaturated alkylidene complexes.

$[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]BF_4$ is prepared by treating $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ (1.9 g, 6.6 mmoles) with $NOBF_4$ (0.55 g, 4.7 mmoles) in 3/1 benzene/methanol solution at 25°C. A rapid color change from orange to deep blue and vigorous gas evolution is observed. After evaporating the solvent under vacuum, the residue is extracted with dichloromethane and filtered. Upon addition of diethyl ether and cooling to −78°C, $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]BF_4$ crystallizes as air-stable, blue-black crystals (1.77 g, 87%). Anal. Found: C, 40.17; H, 4.76; N, 2.36. $C_{21}H_{30}NO_2Rh_2BF_4$ calcd.: C, 40.57; H, 4.87; N, 2.26%.

The presence of bridging carbonyl and nitrosyl ligands is evident in the com-

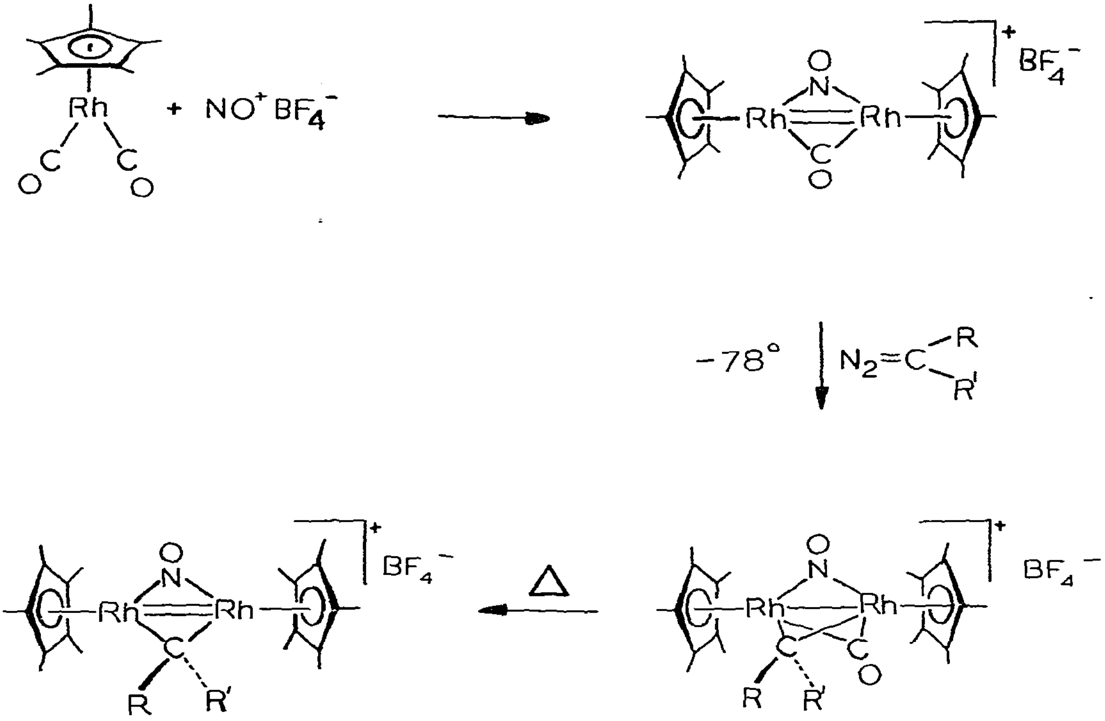

TABLE 1

IR AND ^{1}H NMR DATA FOR $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]BF_4$ AND $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CRR')]BF_4$

Compounds	IR (cm^{-1})^a	^{1}H NMR (δ)^b
$[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]BF_4$	1867(s), 1545(s)	1.74(s)
$[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CH_2)]BF_4$	1551(s)	1.78(s, 30H) 12.32(m, 2H)
$[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CHCH_3)]BF_4$	1540(s)	1.70(s, 30H) 3.33(d, 3H) 13.30(q, 1H)
$[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CHPh)]BF_4$	1544(s)	1.57(s, 30H) 7.44(m, 5H) 13.00(m, 1H)
$[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CPh_2)]BF_4$	1541(s)	1.15(s, 30H) 7.28(m, 10H)

^{a}For solutions in dichloromethane. ^{b}For solutions in deuterochloroform.

pound's infrared spectrum (see Table 1). A single pentamethylcyclopentadienyl resonance is observed in its ^{1}H NMR spectrum. The structure is formulated with a formal rhodium—rhodium double bond, as in the case of $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$ [2].

Addition of slight excesses of ethereal N_2CHR (R = H, Me, Ph) to dry dichloromethane solutions of $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]BF_4$ at —78° C results in red solutions, presumably of $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)(\mu\text{-}CHR)BF_4$. Slight warming (R = H, —20° C; R = Me, —30° C. R = Ph, —60° C) causes elimination of CO and a concomitant color change to deep green. Addition of diethyl ether and cooling to —78° C precipitates the compounds $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CHR)]BF_4$ as green microcrystals (R = H, 73%; R = Me, 54%; R = Ph, 91%). $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CPh_2)]BF_4$ was prepared at 25° C by addition of excess N_2CPh_2 to $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)]BF_4$ and subsequent recrystallization from diethyl ether/dichloromethane at —15° C (67%). At 25° C the methylene and ethylidene compounds decompose as solids within several days and in solution within hours, whereas the benzylidene and diphenylmethylidene compounds are apparently stable indefinitely.

The mass spectrum of each alkylidene compound shows a strong molecular ion peak as well as peaks for the expected fragment ions. A strong bridging-nitrosyl band is observed in the infrared spectrum of each compound (see Table 1). The ^1H NMR resonances of hydrogen atoms bound to the alkylidene carbons appear at very low field. This effect is attributed to the presence of the cationic nitrosyl ligand and to unsaturation. Thus, at —80° C the saturated precursor $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)(\mu\text{-}CH_2)]BF_4$ shows a signal for the methylene protons at δ 9.00 ppm, which is 3 ppm downfield from the analogous signal for the isoelectronic compound $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2(\mu\text{-}CH_2)$. However, the methylene resonance for the decarbonylated compound $[(\eta^5\text{-}C_5Me_2)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CH_2)]BF_4$ is shifted an additional 3 ppm downfield to δ 12.32 ppm. A similarly low field signal is observed for the methylene protons (δ 10.68 ppm) of the closely related unsaturated compound $(\eta^5\text{-}C_5Me_5)_2Co_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ [4].

The facility with which the nitrosyl-carbonyl compounds $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}NO)(\mu\text{-}CO)(\mu\text{-}CRR')]BF_4$ decarbonylate, in comparison with the analogous dicarbonyl compounds $[(\eta^5\text{-}C_5Me_5)Rh(CO)]_2(\mu\text{-}CRR')$, is directly attributable to the labilizing effect of the cationic nitrosyl ligand. Further aspects of the reactivity of this series of unsaturated dirhodium alkylidene complexes are currently being investigated in our laboratory.

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