

Alkylidene Dirhodium Chemistry

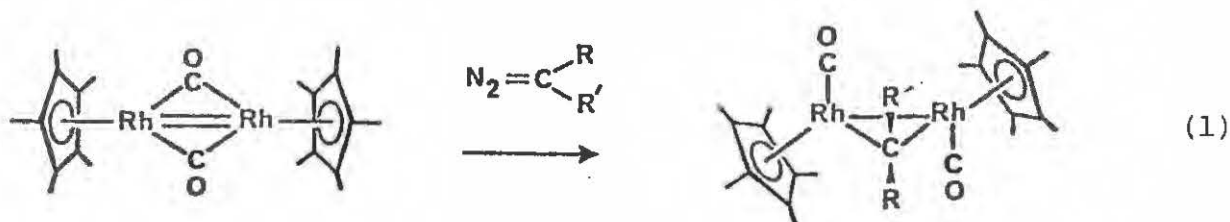
Peter A. Dimas

Final Seminar

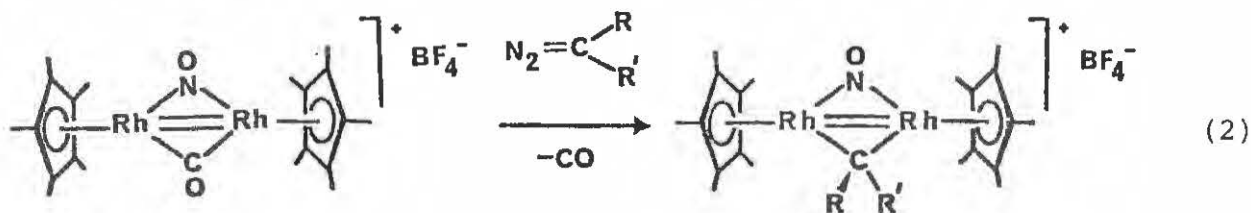
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The synthesis and study of transition metal complexes of new carbon-containing ligands constitute continuing objectives of organometallic chemists. In recent years, dimetal and cluster complexes containing the alkylidene bridge, $\mu\text{-CRR}'$, have attracted considerable attention [1]. This is due, in part, to the implicated role of alkylidene intermediates in surface processes such as the chemisorption of hydrocarbons [2] and the hydrogenation of carbon monoxide [3]. The number of molecular μ -alkylidene complexes has proliferated in a relatively short period of time. Current efforts are focused on examining the reactivity of these complexes.

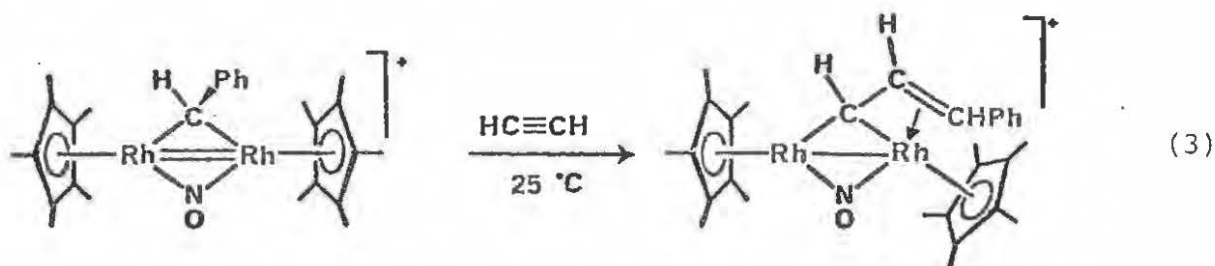
We have found that unsaturated dirhodium compounds react with diazoalkanes to give μ -alkylidene compounds. This synthetic approach, which is analogous to the cyclopropanation reaction of organic chemistry, is based on the isolobal relationships between metal-metal double bonds and alkenes. Thus $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CO})]_2$ reacts rapidly with diazo compounds at room temperature to form $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\text{CO})_2(\mu\text{-CRR}')]_2$ quantitatively. Thermolysis of one member of this set results in decarbonylation to form an unsaturated compound (see reaction 1) [4].



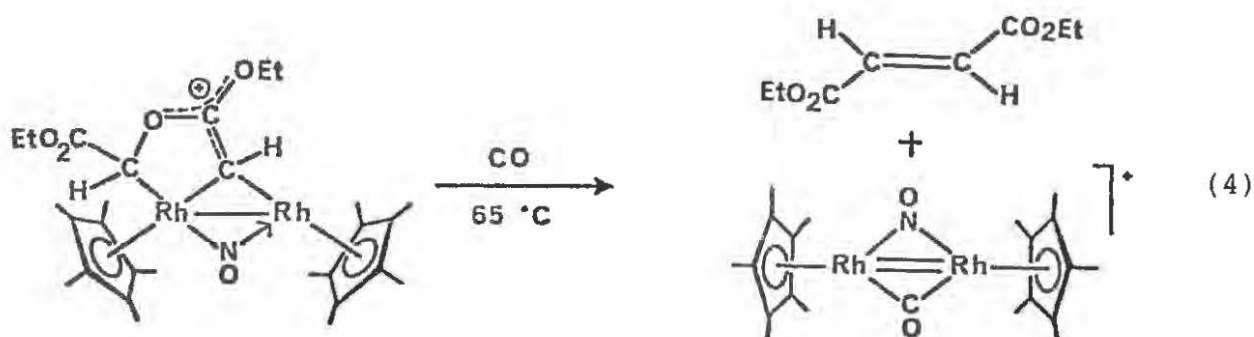
Another unsaturated complex, $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-NO})(\mu\text{-CO})]\text{BF}_4$, has been prepared from $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2]$ and NOBF_4 . It also reacts with diazo compounds (-78°C) to form μ -alkylidene complexes which decarbonylate upon warming to room temperature resulting in a novel series of unsaturated μ -alkylidene compounds (reaction 2) [5].



These compounds provide us with a unique opportunity to examine the reactivity of alkylidene groups toward unsaturated hydrocarbon ligands under milder conditions than previously possible. $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-NO})(\mu\text{-CHPh})]\text{BF}_4$ is highly reactive toward acetylene, forming a stable vinylmethylidene compound via alkyne insertion into the metal-alkylidene bonds (reaction 3).

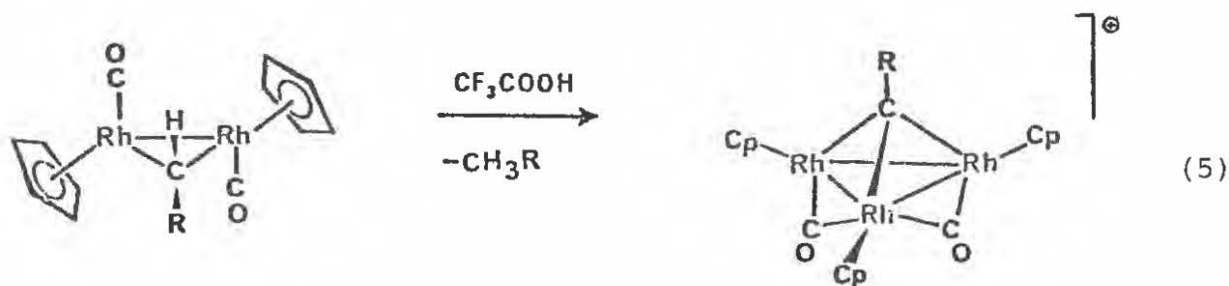


A bis-alkylidene complex has been prepared from $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{-Rh}_2(\mu\text{-NO})(\mu\text{-CO})]\text{BF}_4$ and ethyl diazoacetate. The two alkylidene moieties are condensed into a unique dimetallocycle, resulting in a bridging alkylidene moiety and a terminal one. Heating a solution of this dimetallocycle under a carbon monoxide atmosphere induces coupling of the alkylidene moieties to form an alkene (reaction 4).



Crossover experiments provide evidence for an intramolecular coupling mechanism [6].

An important aspect of the reactivity of alkylidene groups on metal surfaces is their interconversions with alkyl or alkylidyne groups. In order to generate molecular analogs of these transformations we have examined the protonation of several μ -alkylidene complexes. Treatment of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\mu\text{-CHR})]$ ($\text{R} = \text{H}, \text{Me}$) with trifluoroacetic acid causes disproportionation to give CH_3R and the novel cationic alkylidyne clusters $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu\text{-CO})_2(\mu_3\text{-CR})]^+$ (reaction 5) [7].



References

1. Herrmann, W. A. Adv. Organomet. Chem. 1982, 20, 159.
2. a) Anderson, J. R. A.C.S. Div. Petrochem. Preprints 1981, 26, 361.
b) Osterloh, W. T.; Cornell, M. E.; Pettit, R. J. Am. Chem. Soc. 1982, 104, 3759.
3. Rofer-De Poorter, C. K. Chem. Rev. 1981, 81, 447.
4. a) Clauss, A. D.; Dimas, P. A.; Shapley, J. R. J. Organomet. Chem. 1980, 201, C31.
b) Herrmann, W. A.; Bauer, C.; Plank, J.; Kalcher, W.; Speth, D.; Ziegler, M. L. Angew. Chem., Int. Ed. Engl. 1981, 20, 193.
c) Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. J. Chem. Soc., Dalton Trans. 1982, 1309.
5. Dimas, P. A.; Shapley, J. R. J. Organomet. Chem. 1982, 228, C12.
6. Dimas, P. A.; Shapley, J. R.; Rheingold, A. L.; Fultz, W. C., manuscript in preparation.
7. a) Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. J. Am. Chem. Soc. 1980, 102, 7787.
b) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. J. Am. Chem. Soc. 1981, 103, 63.