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Y = CO₂Et) but may only be possible for the one conforma- conformational grounds and on the basis that the appropriate periplanar to the departing Br-ion.

The 1/1 ratios of \hat{C}_5/\hat{C}_6 -ring olefins (Table) obtained from (1b) for the Ni and Co complexes can also be explained on

tion out of three, i.e., where X instead of Me or Y is anti- π -complexes are directly involved in the oxidative addition

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Transition-metal-catalysed Reactions of Diazoesters. Insertion into C-H Bonds of Paraffins by Carbenoids

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Summary Rhodium(II) carboxylates of perfluoroacids are very efficient catalysts for promoting the insertion of carbenes (carbenoids) (generated from diazoesters) into the C-H bonds of alkanes with selectivities which differ from those observed in typical free-carbene processes.

WE have already shown the beneficial influence of strongly electron-withdrawing carboxylate ligands on some Rhmcatalysed carbene reactions (e.g. addition to aromatic molecules1). We report herein the efficiency of rhodium(II) derivatives of strong organic acids (p $K_a < 1$) for promoting, under mild conditions, the insertion of carbenes (carbenoids) generated from diazoesters (Alk-DA) into the C-H bonds of alkanes.

Table 1. Yields of C-H monoinsertion products in the Rh-CF₃catalysed decomposition of EtDA in alkanes.4

Alkane	Insertion yield/%b Alkane `		Insertion yield/%b	
$\begin{array}{c} c-C_{5}H_{10} \\ c-C_{6}H_{12} \\ c-C_{6}H_{11}Me \\ c-C_{7}H_{14} \\ c-C_{8}H_{16} \end{array}$	50 (68°) 78 (90°) 29 ^d 43 (62°) 64	$\begin{array}{l} \text{n-C}_5\text{H}_{12} \\ \text{n-C}_4\text{H}_8\text{Me}_2\text{-}2,3^g \\ \text{n-C}_4\text{H}_9\text{Me-}2^h \\ \text{n-C}_5\text{H}_{11}\text{Me-}2^l \end{array}$	65 (92°) 46 (88,12°) 71 (5,25,66,4°) 68d	

^a Reaction conditions: 22 °C, 100 mmol of cycloalkane or 200 mmol of n-alkane, 3 mmol of EtDA, $2\cdot0$ — $2\cdot2\times10^{-3}$ mmol of Rh-CF₃. Yields were based on EtDA (g.l.c.); addition time 4 h with an automatic syringe. b Average of at least two runs. o Optimized yields at the alkane boiling point. d Mixture of isomers. C-H insertion (%) at C-1 and C-2, respectively. C-H insertion (%) at C-1, C-2, C-3, and C-4, respectively. 2,3-Dimethylbutane. 2-Methylbutane. 2-Methylbutane.

Table 1 summarizes the results obtained with some (cyclo)alkanes and tetrakis(trifluoroacetato)dirhodium(II) (rhodium trifluoroacetate, Rh-CF3) as the catalyst.

The yields were good² and vary inter alia with the reaction temperature (see Table 1 for the effect at the alkane boiling point) and the ratio of substrate to diazoester. When the latter was low (<ca. 20—30), the formation of oligomers of carbene predominated, with fast catalyst deactivation. Although insertion into C-H bonds by carbenoids is an uncommon process,3 several observations indicate that free carbenes are not the active species. Firstly, the RhIIcatalysed C-H insertions into n-pentane exhibit regioselectivities significantly different from those observed in typical free-carbene processes. Indeed, C-H insertions at C-1, C-2, and C-3 of n-pentane were respectively 7, 66, and 27% (catalytic reaction conditions of Table 1), as compared with 38, 45, and 25% when the carbene was photochemically promoted, i.e. catalytic insertion into primary C-H bonds was nearly suppressed. Secondly, competitive experiments between pairs of alkanes showed that, with Rh-CF3 as the catalyst, the high-molecular weight (long-chain) alkane was preferred {e.g. ratio of inserted n-pentane to n-decane 0.5 [equivalent weights, with ethyl diazoacetate (EtDA)]}. A similar trend was also observed with the cycloalkanes and the results are summarized in Table 2.

Moreover, the selectivity of insertion strongly depended on both the diazoester alkoxy-group and the metal counterion. For example, when the diazoester was catalytically decomposed by Rh-CF3 in a mixture of cyclopentane and cyclo-octane (equivalent weights) the relative ratio of inTABLE 2. Selectivities of C-H insertions in intermolecular competitions.a

	Method	Ratio of C-H insertion between cycloalkanes		
Diazoester	of decom- position ^b	C ₆ /C ₈	C_6/C_8	C ₆ /C ₅
MeDA	A, RhCF ₃ B and C	0·13 ca. 1·0	0·3 1·0	1·5 1·0
MeDA + EtDA EtDA	A, RhCF ₃	0.6	0.75	1.3
EtDA	A, RhC ₇ F ₁₁	, 1.8	1.35	

a Catalytic reaction conditions were the same as in Table 1 The relative insertions (%) are corrected for the number of hydrogen atoms. b A, catalyst; B, photochemical, 300 W highpressure Hg lamp, water-cooled Pyrex jacket; C, thermal, sealed ampoules, 150 °C (for photochemically promoted C-H insertions, see also H. Tomioka, M. Itoh, S. Yamakawa, Y. Isawa, J. Chem. Soc., Perkin Trans. 2, 1980, 603)

serted cyclopentane to cyclo-octane was 0.13 with MeDA and 0.6 with EtDA. However, replacement of Rh-CF3 by Rh^{II} perfluoro-octanoate (Rh-C₇F₁₅) promoted a dramatic reversal of selectivity, the ratio changing to 1.8.

Preferential complex solvation by one of the alkanes could account for the surprising selectivities observed in competitive experiments. The alterations in the relative selectivities brought about in competition experiments by a simple homologation of the diazoester alkoxy-group are unique and are indicative of the importance of carbenoidsubstrate lipophilic interactions, ‡ a finding which is substantiated by the sensitivity of the reaction to alkane substitution (e.g. competition between methylcyclohexane and cyclohexane with EtDA and Rh-CF3 gave a C-H insertion ratio of 0.7; competition between n-pentane and 2,3dimethylbutane gave a C-H insertion ratio of 1.45).

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Synthesis, Dynamic Behaviour, and Molecular Structures of μ -Methylene Platinumtriosmium Complexes; X-Ray Crystal Structures of Two Isomers of $[Os_3Pt(\mu-H)_2(\mu-CH_2)(CO)_{10}\{P(C_6H_{11})_3\}]$

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Summary Treatment of $[Os_3Pt(\mu-H)_2(CO)_{10}\{P(C_6H_{11})_3\}]$ with diazomethane affords, under kinetic control, a single isomer $[Os_3Pt(\mu-H)_2(\mu-CH_2)(CO)_{10}\{P(C_6H_{11})_3\}]$, which in solution isomerises (days) to a second isomer; the structures in the solid state of both isomers have been determined by X-ray crystallography, and those in solution by ¹H and ²H n.m.r. spectroscopy.

Metal complexes containing bridging methylene (μ-CH₂) ligands are still relatively rare, and except for [Os₃(µ-H)₂(µ-CH₂)(CO)₁₀]¹ are limited to bimetallic compounds of Mn,² Co,3 Rh,4 Fe,5 Ru,6 and Pt.7 Interest in these species has been stimulated by the idea that μ -CH₂ groups on a metal surface are intermediates in the conversion of CO into hydrocarbons in Fischer-Tropsch chemistry.8 The observation that the 58-electron (unsaturated) closo-cluster $[{\rm Os_3Pt}(\mu\text{-H})_2({\rm CO})_{10}\{{\rm P(C_6H_{11})_3}\}]$ $({\bf 1a})$ readily adds a molecule of CO suggested that it would also react with CH2N2 to afford the first tetranuclear metal complex with a μ -CH₂ ligand.

Treatment of (1a) [0 °C, tetrahydrofuran (THF)] with excess of CH₂N₂ in Et₂O led to rapid nitrogen evolution. Chromatography of the mixture gave a product which on recrystallisation (toluene-light petroleum) afforded two isomeric complexes $[Os_3Pt(\mu-H)_2(\mu-CH_2)(CO)_{10}\{P(C_6H_{11})_3\}]$ which were separated as orange (3a) and red (3b) crystals

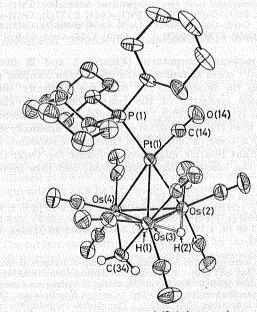


FIGURE 1. Molecular structure of (3a) (orange isomer). Bond lengths Pt(1)-Os(2) 2·730(1), Pt(1)-Os(3) 2·814(1), Pt(1)-Os(4) 2·826(1), Os(2)-Os(3) 2·954(1), Os(2)-Os(4) 2·941(1), Os(3)-Os(4) 2·826(1), Os(3)-C(34) 2·143(8), Os(4)-C(34) 2·118(8), mean Os-H 1.8(1) Å; $\angle Os(3)-C(34)-Os(4)$ 83.1(3)°.

 $[\]dagger$ All the compounds described in this work were identified by g.l.c. (including analysis on capillary columns, 50 m imes 0.25 mm, FFAP), by comparison with authentic samples synthesized by independent methods, and by coupled g.l.c.-m.s. When needed, corrections were made for the relative responses to the catharometer.