

Y = CO₂Et) but may only be possible for the one conformation out of three, *i.e.*, where X instead of Me or Y is anti-periplanar to the departing Br⁻ ion.

The 1/1 ratios of C₅/C₆-ring olefins (Table) obtained from (1b) for the Ni and Co complexes can also be explained on

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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 Rh^{II}-catalysed carbene reactions (*e.g.* addition to aromatic molecules¹). We report herein the efficiency of rhodium(II) derivatives of strong organic acids (*pK_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-CF₃-catalysed decomposition of EtDA in alkanes.^a

Alkane	Insertion yield/% ^b	Alkane	Insertion yield/% ^b
c-C ₆ H ₁₀	50 (68 ^c)	n-C ₅ H ₁₂	65 (92 ^c)
c-C ₆ H ₁₂	78 (90 ^c)	n-C ₄ H ₉ Me ₂ -2,3 ^e	46 (88, 12 ^e)
c-C ₆ H ₁₁ Me	29 ^d	n-C ₄ H ₉ Me-2 ^h	71 (5, 25, 66, 4 ^f)
c-C ₇ H ₁₄	43 (62 ^c)	n-C ₅ H ₁₁ Me-2 ^l	68 ^d
c-C ₈ H ₁₆	64		

^a Reaction conditions: 22 °C, 100 mmol of cycloalkane or 200 mmol of n-alkane, 3 mmol of EtDA, 2.0–2.2 × 10⁻³ 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. ^c Optimized yields at the alkane boiling point. ^d Mixture of isomers. ^e C-H insertion (%) at C-1 and C-2, respectively. ^f C-H insertion (%) at C-1, C-2, C-3, and C-4, respectively. ^g 2,3-Dimethylbutane. ^h 2-Methylbutane. ^l 2-Methylpentane.

† All the compounds described in this work were identified by g.l.c. (including analysis on capillary columns, 50 m × 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.

conformational grounds and on the basis that the appropriate π-complexes are directly involved in the oxidative addition step.

(Received, 16th April 1981; Com. 453.)

TABLE 2. Selectivities of C-H insertions in intermolecular competitions.^a

Diazoester	Method of decomposition ^b	Ratio of C-H insertion between cycloalkanes		
		C ₅ /C ₈	C ₆ /C ₈	C ₆ /C ₅
MeDA	A, RhCF ₃	0.13	0.3	1.5
MeDA + EtDA	B and C	ca. 1.0	1.0	1.0
EtDA	A, RhCF ₃	0.6	0.75	1.3
EtDA	A, RhC ₇ F ₁₅	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 high-pressure 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

(Received, 30th March 1981; Com. 365.)

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Synthesis, Dynamic Behaviour, and Molecular Structures of μ-Methylene Platinumtriosmium Complexes; X-Ray Crystal Structures of Two Isomers of [Os₃Pt(μ-H)₂(μ-CH₂)(CO)₁₀{P(C₆H₁₁)₃}]

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Summary Treatment of [Os₃Pt(μ-H)₂(CO)₁₀{P(C₆H₁₁)₃}] with diazomethane affords, under kinetic control, a single isomer [Os₃Pt(μ-H)₂(μ-CH₂)(CO)₁₀{P(C₆H₁₁)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 observation⁹ that the 58-electron (unsaturated) *closo*-cluster [Os₃Pt(μ-H)₂(CO)₁₀{P(C₆H₁₁)₃}] (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 [Os₃Pt(μ-H)₂(μ-CH₂)(CO)₁₀{P(C₆H₁₁)₃}] which were separated as orange (3a) and red (3b) crystals

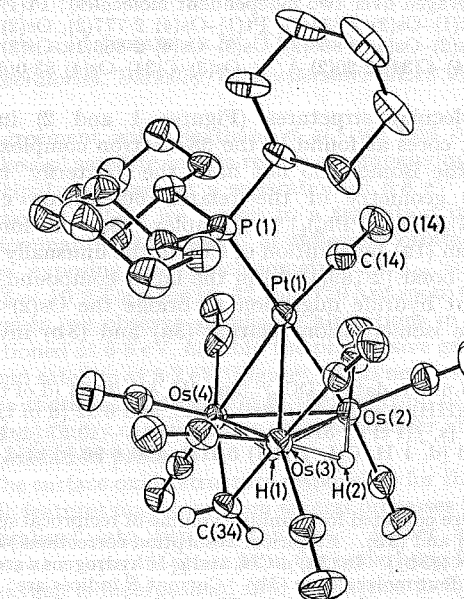


FIGURE 1. Molecular structure of (3a) (orange isomer). Bond lengths Pt(1)–Os(2) 2.730(1), Pt(1)–Os(3) 2.814(1), Pt(1)–Os(4) 2.826(1), Os(2)–Os(3) 2.954(1), Os(2)–Os(4) 2.941(1), Os(3)–Os(4) 2.826(1), Os(3)–C(34) 2.143(8), Os(4)–C(34) 2.118(8), mean Os–H 1.8(1) Å; ∠ Os(3)–C(34)–Os(4) 83.1(3)°.