

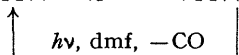
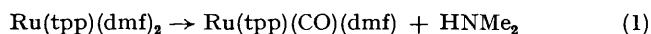
Catalytic Decarbonylation of Aldehydes using Ruthenium(II) Porphyrin Systems

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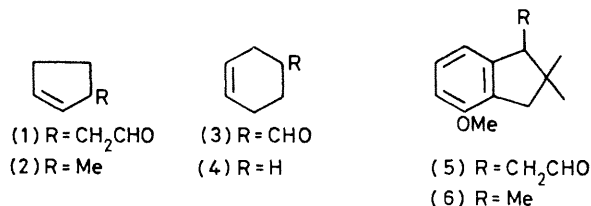
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Summary Extremely efficient decarbonylation of aromatic and aliphatic aldehydes has been accomplished catalytically under ambient conditions using solutions of bis(triphenylphosphine) (tetraphenylporphyrinato)-ruthenium(II).

ALTHOUGH stoichiometric decarbonylation of aldehydes and acid chlorides is readily achieved using platinum metal complexes, especially of ruthenium, palladium, and rhodium,¹ it is generally difficult to remove the coordinated carbonyl from the resulting complex either thermally¹ or photolytically² (conditions that decompose sensitive substrates), and as a result few cases of such catalytic decarbonylation have been reported.³ An observed catalytic photodecarbonylation of dimethylformamide (dmf) at a Ru(tpp) centre [reaction (1), tpp = dianion of tetraphenylporphyrin]⁴ has led indirectly to the discovery of a remarkably efficient catalyst for a purely thermal decarbonylation of aldehydes under ambient conditions [reaction (2)].



The most effective system is formed by dissolving about 10^{-6} mol of $[\text{Ru(tpp)(Ph}_3\text{P)}_2]^5$ in 1 ml of CH_2Cl_2 , and adding this to about 50 ml MeCN or PhCN containing the aldehyde (up to 0.5 M), and Bu^n_3P (phosphine:Ru ca. 10:1). Decarbonylation of the aldehyde occurs on standing, after activating the system by stirring under 1 atm of CO for a few seconds. Warming to ca. 50 °C, and replacement of the CO by argon, led to faster decarbonylation, and formation of toluene from phenylacetaldehyde, for example, occurred with a turn-over number of $>10^4$ in 30 min (see Table).



The decarbonylations, which do not appear to be effected by light, are reasonably selective with aromatic aldehydes, yielding the expected product; however, significant amounts of other products are obtained with non-aromatic substrates (*e.g.*, cyclohexanecarbaldehyde gives methylcyclopentane and small amounts of n-hexane, as well as the

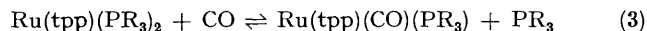
TABLE Decarbonylation of aldehydes

Substrate	Major product (%) ^a	Conversion (time) ^b	Turnover ^c
PhCHO	Benzene (100)	10(5)	10
PhCH ₂ CHO	Toluene (95) ^d	30(1), 90(4)	10 ³ ^e
C ₆ H ₁₁ CHO	C ₆ H ₁₂ (60) ^f	30(1), 50(18), 90(50)	200
2-Ethylbutanal	n-Pentane (85) ^g	30(1)	10 ³
Heptanal	n-Hexane (65) ^h	10(1)	10 ²
(1)	(2) (90) ^g	10(1), 30(36), 90(150)	10 ²
(3)	(4) (70) ⁱ	10(1), 20(12)	10 ²
(5)	(6) (70) ^g	20(5)	10 ²

^a Identified by g c -m s and/or n m r spectroscopy % refers to amount of major species in the decarbonylation products at the highest conversion noted ^b % Conversion of aldehyde, time in h ^c For the first hour at ambient temperature, based on loss of aldehyde and/or formation of product as detected by v p c ^d Small amounts of benzene also detected ^e At ca 50 °C, turnover $5 \times 10^4 \text{ h}^{-1}$ ^f Methylcyclopentane (35%), some n-hexane also detected ^g Other products not yet identified ^h An isomer and some hexene also detected ⁱ Cyclohexane also detected

expected cyclohexane) At ambient temperatures, long reaction times (≥ 50 h) are usually required for 90% decarbonylation, although up to 30% reaction is commonly achieved in 1 h Cinnamaldehyde was not effectively decarbonylated

The nature of the catalyst remains uncertain, species present during decarbonylation can be monitored by absorption peaks in the Soret region The bis(phosphine) systems, which show λ_{max} at 435 nm (Ph₃P) or 437-(Bu₃P), can react reversibly with CO to give the carbonyl-phosphine [414 nm (Ph₃P), and 415(Bu₃P)], reaction (3), and the carbonyls are formed by treatment of the bis-



(phosphine) systems with an aldehyde, presumably in a stoichiometric reaction [cf reaction (2)] However, the Ru(tpp)(PR₃)₂ and Ru(tpp)(CO)(PR₃) complexes themselves⁶ are significantly less active than the mixed *in situ* PPh₃/

PBu₃ system The active system requires Soret maxima both in the 415 and 435 nm regions, PBu₃ is much more effective than PPh₃ for displacement of co-ordinated CO [equilibrium (3)], and it seems that both phosphine ligands play active roles

The familiar decarbonylation mechanism^{1,3} involving a concerted oxidative-addition of aldehyde, CO migration (with subsequent elimination), and reductive-elimination of product, would seem with metallocporphyrins to require co-ordination numbers higher than six Alternative mechanisms involving heterolytic or homolytic cleavage of the aldehyde C-H bond are being considered, particularly in view of the product mixture obtained with the non-aromatic substrates

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³ D H Doughty M F McGuiggan, H Wang and L H Pignolet in 'Fundamental Research in Homogeneous Catalysis' Vol 3, ed M Tsutsui Plenum Press New York 1979, p 909

⁴ B R James A W Addison M Cairns, D Dolphin, N P Farrell, D R Paulson, and S Walker, in 'Fundamental Research in Homogeneous Catalysis' Vol 3 ed M Tsutsui Plenum Press, New York, 1979, p 751

⁵ T Boschi, G Bontempelli and G-A Mazzocchin, *Inorg Chim Acta*, 1979, **37**, 155

⁶ G Domazetis D Dolphin and B R James unpublished results