ation of **2** and **3** probably affords the yet undetected alkyl–acyl intermediate **5a**[8] which appears to collapse by reductive elimination to the ketone and a coordinatively unsaturated iron(0) complex.[10] Protonation of the alkyl and acyl intermediates **1**, **2**, and **3** affords the corresponding alkanes and aldehydes. The latter reaction is the basis of the aldehyde synthesis which we reported earlier.[2]

Specific examples of ketone syntheses listed in Table I illustrate the following points.[11] Since both alkylations in eq a, b, and c are $S_N2$ reactions, substrate limitations are understandable in view of the apparent order of decreasing nucleophilicity: $[Fe(CO)_4]^{2-} >$ $[RFe(CO)_4]^- > [(RCO)Fe(CO)_3(P(C_6H_5)_3)]^- > [(RCO)$-$Fe(CO)_4]^-$. In the first alkylation primary bromides, iodides, and tosylates and secondary tosylates can be used, but the second stage requires more reactive alkylating agents such as primary iodides or tosylates, benzylic halides, or $\alpha$-chloro ethers. To ensure maximum yields an excess of the second alkylating agent must be employed, especially for methods c and d which involve the poorest iron nucleophile. Secondary tosylates are preferred over the bromides to minimize eliminations.[12]

The most remarkable and potentially useful feature of the $[Fe(CO)_4]^{2-}$ reagent is its toleration of organic functional groups. This is illustrated (Table I) by the conversion of a 5-bromo ester into a 6-keto ester.

Method c is stereospecific, and it is likely that the other methods will also be so. $(S)$-$(+)$-2-Octyl tosylate $([\alpha]^{25}D +7.96°, 99\%$ ee) afforded $(R)$-$(-)$-3-methyl-2-nonanone $([\alpha]^{25}D -12.03°, 99\%$ ee) with overall inversion at the chiral carbon.[14] In view of the well-known inversion in $S_N2$ reactions and the recently established retention in an alkyl–acyl insertion,[15] we suppose that **1** is formed with inversion and that the transformation to **3** takes place with retention.

(8) It is possible that the reaction proceeds *via* a neutral carbene complex, $(OC)_4FeC(OR')R$, but similar carbene complexes have been prepared[9] and appear to be too stable thermally to account for our mild ketone synthesis.

(9) E. O. Fischer and C. G. Kreiter, private communication.

(10) The purported intermediate in eq c, $Fe(CO)_4$, trimerizes to $Fe_3$-$(CO)_{12}$ when free CO is not present.

(11) All reactions were conducted under a nitrogen atmosphere. In a typical preparation 2.16 g (10.3 mmol) of ethyl 5-bromovalerate was added to a solution of 2.37 g (11.1 mmol) of $Na_2Fe(CO)_4$ in 30 ml of *N*-methyl-2-pyrrolidone (distilled from $CaH_2$), the reaction stirred for 1 hr, and 2.4 ml (30.0 mmol) of ethyl iodide added. After 24 hr the solution was diluted with ether, washed three times with brine, dried, and filtered, and the ether was removed with a rotary evaporator. The residue was placed on a short column (130 g of silica gel) and washed free of the colored iron byproducts with hexane, and the product removed with 50% ether–hexane. Fractional distillation gave 1.41 g (74%) of ethyl 6-ketooctanoate.

(12) The basicity of $[Fe(CO)_4]^{2-}$ is estimated to be about that of $[OH^-]$ on the basis of $pK_a$ values reported[13] for the corresponding hydrides.

(13) W. Hieber and W. Hubel, *Z. Elecktrochem.*, **57**, 235 (1953).

(14) The configuration of $(R)$-$(-)$-3-methyl-2-nonanone was established by Baeyer–Villiger degradation to 2-acetoxyoctane which was compared with an authentic sample prepared from $(S)$-$(+)$-2-octanol.

(15) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **91**, 4313 (1969).

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## Resin-Bound Transition Metal Complexes

*Sir:*

Organic reactions in which one component is fastened to a porous solid support offer strategic synthetic advantages in the dilution[1] or isolation[2] of that component and the removal of byproducts.[3] Homogeneous transition metal catalysts bound to a resin may also exhibit properties different from those in solution. For example, a rhodium hydrogenation catalyst attached to polystyrene exhibits selectivity toward smaller olefins.[4,4a] Since the active forms of homogeneous catalysts are unsaturated,[5] immobilization on a solid support might prevent self-aggregation affording high concentrations of unsaturated complexes. As is shown below, this effect will be difficult to achieve with phosphine-substituted polystyrene because of the pronounced tendency of such polymeric ligands to chelate.

Resin-substituted triphenylphosphine **1** was prepared from cross-linked polystyrene (Biobeads SX-2, 2% crosslinking) by sequential bromination ($Br_2$, $FeBr_3$), lithiation (*n*-BuLi, THF), and treatment with $(C_6H_5)_2$-PCl. The following experiments with **1** employed 1.2 mmol of P/g corresponding to 10% ring substitution. Treatment of **1** with the rhodium(I) or iridium(I) complexes, **2**, afforded the resin-bound complexes, **3**, releasing two $P(C_6H_5)_3$ per metal atom



1
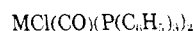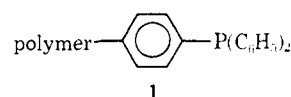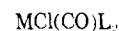
| $MCl(CO)(P(C_6H_5)_3)_2$ | $MCl(CO)L_2$ |
|---|---|
| **2a**, M = Rh | **3a**, L = 1; M = Rh |
| **b**, M = Ir | **b**, L = 1; M = Ir |

introduced into the polymer.[6] Similarly two $P(C_6H_5)_3$ and one $CH_2$=$CH_2$ were displaced from **4** affording the red polymeric complex **5**, an analog of the Wilkinson hydrogenation catalyst.[7] In these and similar cases, intermediate levels of coordination per metal atom in the polymer by resin-bound phosphine could not be achieved either by varying the ratio of starting complex to resin or the level of phosphine incorporated[8] in the resin. That nonstatistical functionalization

(1) R. L. Letsinger, M. J. Kornet, V. Mahadevan, and D. M. Jermia, *J. Amer. Chem. Soc.*, **86**, 5163 (1964).

(2) (a) I. T. Harrison and S. Harrison, *ibid.*, **89**, 5724 (1967); (b) J. I. Crowley and H. Rapoport, *ibid.*, **92**, 6363 (1970).

(3) R. B. Merrifield, *Fed. Proc.*, **21**, 412 (1962); *J. Amer. Chem. Soc.*, **85**, 2149 (1963); **86**, 304 (1964).

(4) R. H. Grubbs and L. C. Kroll, *ibid.*, **93**, 3062 (1971).

(4a) NOTE ADDED IN PROOF. Other resin-bonded catalysts have been described: Mobil Oil, U. S. Patent 1,800,371 (1969); British Petroleum Co., Belgian Patents 739,607 and 739,609.

(5) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).
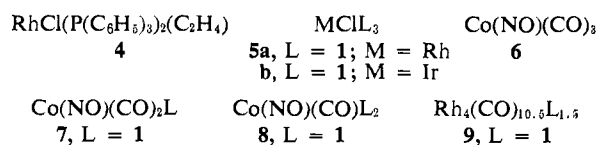
(6) These quantities were determined by analysis of the filtrates from reactions using measured quantities of **1** and the homogeneous complex. A small portion of resin phosphine sites were too sterically hindered to act as ligands. Resin-bound complexes exhibited the same $\nu_{CO}$ and colors as their homogeneous counterparts.

(7) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(8) Phosphine substitution levels down to 2% of the benzene rings in the resin were employed with similar results. Analytical errors become correspondingly larger at these low levels.

leading to pockets of highly substituted resin was not the cause of this chelation was demonstrated by carrying out the above experiments with the same result using a phosphine-substituted "popcorn" copolymer[1] prepared from styrene (0.9 mmol), p-bromostyrene (0.1 mmol), and divinylbenzene (0.002 mmol). The most plausible explanation is that the polymer chain is sufficiently mobile, especially when the resin is solvent swelled, to bring nonadjacent sites together.[9]

In cases where tertiary phosphines are not displaced and monosubstitution is kinetically favored resin chelation does not result. For example, treatment of [Rh(COD)Cl]₂ with 1 yielded a 1:1 resin complex by splitting the chloro bridge. Similarly 1 equiv of **6** reacted with 2 equiv of **1** under mild conditions ($C_6H_5$, 25°) to form the 1:1 complex **7** ($\nu_{CO}$ 2022, 1965; $\nu_{NO}$ 1750). However, further heating (70°, 24 hr, diglyme) converted **7** into the 1:2 complex **8** ($\nu_{CO}$ 1940; $\nu_{NO}$ 1700 cm$^{-1}$).[10]

RhCl(P(C₆H₅)₃)₂(C₂H₄)  MClL₃  Co(NO)(CO)₃
**4**  **5a**, L = 1; M = Rh  **6**
      **b**, L = 1; M = Ir

Co(NO)(CO)₂L  Co(NO)(CO)L₂  Rh₄(CO)₁₀.₅L₁.₅
**7**, L = 1  **8**, L = 1  **9**, L = 1

The resin-bonded complexes exhibit normal reactions. For example, **3b** reacts with p-nitrobenzoyl azide to afford a resin-bound N₂ complex, $\nu_{N_2}$ 2095. Treatment of **3b**, **5a**, or **5b** with hydrogen afforded the spectral changes expected for oxidative addition. The resin-bound mononuclear hydrogenation catalysts **5a,b** were superior to their homogeneous analogs only in catalyst lifetime and ease of product separation.

Novel polynuclear catalysts were prepared by treating **1** with the readily substituted Rh₄(CO)₁₂ and Rh₆-(CO)₁₆.[11] Aerial oxidation (accelerated by light) led to the disappearance of $\nu_{CO}$; H₂ (1 atm, THF) afforded active metal particles of extremely small size, presumably 4 and 6 Rh atoms, respectively. The substance derived from Rh₆(CO)₁₆ catalyzed the hydrogenation of arenes at 25° and 1 atm of H₂, exhibiting reactivity and substrate selectivity similar to Engelhard's 5% Rh/Al₂O₃,[12] whereas that derived from Rh₄(CO)₁₂ exhibited diminished activity which we attribute to Rh₆(CO)₁₆ formed spontaneously in solutions of Rh₄-(CO)₁₂. Evidence that the polymer prevents aggregation is afforded by comparing reactions of these catalysts with CO: from the Rh₄ catalyst over 50% of the Rh was removed as Rh₄(CO)₁₂; from the Rh₆ catalyst a small amount of Rh₄(CO)₁₂ and much Rh₆(CO)₁₆ were obtained at <40 psi; and from 5% Rh/Al₂O₃[13] only a barely detectable amount of Rh₄(CO)₁₂ was obtained after 24 hr at >1000 psi. Polymer-free Rh₄(CO)₁₁-

(9) More highly cross-linked polystyrene resins were employed: Biobeads SX-12 and Rohm and Haas XAD-2 and XE-305. Substantial amounts of phosphine could only be introduced into XE-305 but 2 mequiv of triphenylphosphine was liberated for each milliequivalent of **2b** taken up.

(10) (a) R. F. Heck, J. Amer. Chem. Soc., **85**, 657 (1963); (b) E. M. Thorsteinson and F. Basolo, Inorg. Chem., **5**, 1691 (1966).

(11) (a) R. Whyman, Chem. Commun., 230 (1970); (b) B. L. Booth, M. J. Else, R. Fields, and R. N. Hazeldine, J. Organometal. Chem., **27**, 119 (1971).

(12) P. N. Rylander and L. Hasbrouck, "Technical Bulletin," Vol. X, No. 2, Engelhard Industries, Murray Hill, N. J., 1969, p 50.

(13) Hydrogen adsorption studies of this catalyst by H. Uchida showed 43% dispersion. Assuming a cubic shape, this corresponds to an average particle size of 40 or 80 Å corresponding to each surface Rh taking up one or two H atoms.

(P(C₆H₅)₃) similarly oxidized and reduced also catalyzed arene reduction but failed to give Rh₄(CO)₁₂ upon CO treatment suggesting that irreversible aggregation to larger metal units occurred without the use of the polymeric ligand.

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## New Synthetic Reactions. Transfer Alkylations

*Sir:*

Enolates derived from unsaturated carbonyl systems are potentially ambident in their behavior toward carbon alkylation.[1] Conceptually, an alkylating agent may add at the $\alpha$, $\gamma$, $\epsilon$, etc., carbon (eq 1); practically
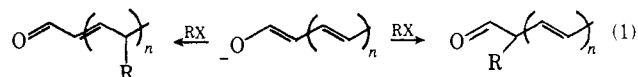
C-alkylation occurs selectively at the $\alpha$-carbon—the carbon bearing the highest negative charge density. In conjunction with synthetic studies directed toward sesquiterpene antibiotics, we required large quantities of diester acid **1**. Thus, we desired a reaction introducing

**1**
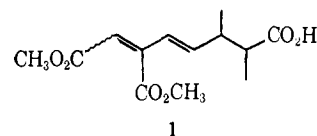
an $\alpha$-methylacetic acid unit at one of the more remote positions (*i.e.*, $\gamma$, $\epsilon$, etc.) in a polyenolate. Here we wish to report a convenient solution to this problem.

Equation 2 exemplifies the concept. Treatment of a
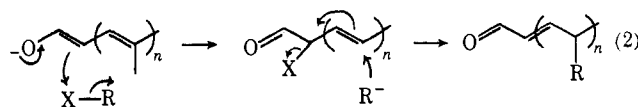
polyenolate with an alkyl halide that undergoes displacement at halogen generates a carbanion and a new 2-halo-$\beta$,$\gamma$-unsaturated ketone. Recombination of these partners by SN2' like attack generates net $\gamma$ or $\epsilon$ alkylation. We term this process transfer alkylation. The appropriate choice of an alkylating agent is crucial. Bromomalonates are ideal because of their ability to act as bromonium sources and their ease of conversion to acetic acids. Three bromomalonates (**2**, **3**, and **4**) were screened.[2–4]

(1) (a) For a discussion of enolate alkylation, see: H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 190–192. (b) This reaction may also be termed an oxidative Michael reaction.