regarding the specific type of reaction observed here it should be noted that (CF$_3$P)$_4$ reacts quantitatively with CH$_3$PH$_2$ to give CF$_3$PH$_2$ and (CH$_3$P)$_5$[14a] but the course followed by the reaction, when the phosphine and cyclophosphine are identically substituted, was not considered. The first isolated disecondary diphosphine (CF$_3$PH)$_2$[2a] has been reported to decompose above 225°, giving mainly (CF$_3$P)$_4$ and CF$_3$PH$_2$, but the reverse reaction was apparently not observed. We are presently investigating some other mixtures (RP)$_n$–RPH$_2$ to test the generality of the equilibrium giving rise to I.

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A New Simple Method for Rapid Tritium Labeling of Organics Using Organoaluminum Dihalide Catalysts

Sir:

We have recently published[1] a method for rapid deuteration of aromatic compounds using organoaluminum dihalide catalysts promoted by a trace of water. Equilibration of deuterium between two aromatic compounds such as benzene-d_6 and bromobenzene is attained within minutes at room temperature, the exchange being highly selective for aromatic hydrogen atoms and not subject to steric effects in the aromatic ring. D$_2$O is not a suitable source of deuterium in such deuteration reactions because the catalyst is rapidly hydrolyzed, although small traces of water promote the catalyst activity.

We now report that the same organoaluminum dihalide catalysts with tritiated water as the isotope source and catalyst promoter may be used for instantaneous tritium labeling of a variety of organic compounds.

When tritium labeling is the objective, as distinct from deuterium labeling, traces of high specific activity tritiated water may be used to hydrolyze a solution of the organoaluminum dihalide catalyst in an organic substrate. Adequate tritium labeling of the substrate accompanies this hydrolysis. This method is not suitable for deuterium labeling since substantial exchange with D$_2$O and not just hydrolysis of some catalyst complex is necessary to achieve reasonably high deuterium isotope ratios. A range of organoaluminum halides has been used as catalysts, ethylaluminum dichloride being the most satisfactory.

Table I. Compounds Labeled by Tritiated Water Using Ethylaluminum Dichloride Catalyst[a]

% incorporation of tritium into organic compound[b] 10–100%	1–10%	0.1–1%
Benzene	Furan	Cyclohexene
Toluene	Cyclohexanone	
Naphthalene	1-Methylcyclopentene	
Anthracene	1-Methylcycloheptene	
Pyrene	Triphenylamine	
Azulene		
Anisole		
Pyrrole		
Chlorobenzene		

[a] Reaction conditions: room temperature, 2 min, 50 mCi of HTO. [b] Expressed as per cent of total tritium in reaction mixture.

Table I shows representative compounds labeled by the present technique in which ethylaluminum dichloride (0.01 g) was added by syringe to the organic substrate (0.2 g) under dry nitrogen, and the solution treated with a drop of tritiated water (0.01 g, 5 Ci/g). After approximately 2 min, ordinary water (1 ml) was added to ensure complete hydrolysis of the catalyst. The organic product was analyzed simultaneously for chemical and radiochemical products by means of a gas–liquid chromatograph coupled to an ion-chamber radioactivity detector assembly. In no system was any radioactive or nonradioactive product detected other than the labeled parent compound. The results in Table I are expressed as the percentage of the added tritium that is incorporated into the organic compound. For the conditions stated above, the specific activities of products ranged from 18 mCi/mmol for benzene to 0.2 mCi/mmol for cyclohexene. Higher specific activities are obtained if higher specific activity HTO is used.

Of the hydrocarbons studied, aromatics were labeled with high efficiency while alkenes were tritiated to a lesser extent (Table I). Saturated hydrocarbons have not been successfully labeled by the present technique. A variety of substituted hydrocarbons labeled readily.

Detailed studies of the orientation of isotope after labeling have not yet been carried out. However, oxidation of labeled toluene to benzoic acid with complete retention of tritium activity showed toluene was labeled only in the ring. Nitration of the toluene followed by gas-chromatographic analysis of the mixed nitration products showed a random distribution of tritium in the aromatic ring. This result is in accord with the high selectivity for aromatic proton exchange and absence of steric effects within the aromatic ring observed in the deuteration studies on a wide variety of compounds.[1]

The work of Balaban and coworkers[2–4] may be related to this present study. They labeled a range of organic compounds by using aluminum chloride in prolonged exchange with tritiated water present at a molar concentration about half that of the catalyst. With benzene, exchange was complete in 1.5 hr at room temperature, but with chlorobenzene exchange was incomplete even after 3 hr at 100°. A variety of other compounds exhibited varying degrees of exchange after prolonged times at elevated temperatures.

The present method, using organoaluminim dihalides, is much faster for aromatic compounds than that proposed by Balaban, *et al.*[2] This is exemplified by the instantaneous tritiation of chlorobenzene at room temperature in the present method. Speed of labeling

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is of the utmost importance in tritiation reactions, especially to high specific activities, since degradation of the organic substrate through exposure to high tritium β radiation fields must be minimized. Thus, the present catalytic method should offer significant advantages over other radiation-induced[5,6] and catalytic procedures[7] for tritium labeling because of its simplicity, speed, selectivity for aromatic protons, and freedom from side reactions.

A plausible mechanism for the labeling reaction would involve the formation of a complex between the catalyst and the organic compound, possibly through a π-associative type species as proposed for other catalytic exchange systems.[8,9] Hydrolysis of the complex with tritiated water could be accompanied by a proton transfer resulting in incorporation of tritium into the organic substrate.

Acknowledgment. We thank the Australian Research Grants Committee and the Australian Institute of Nuclear Science and Engineering for the support of the research at The University of New South Wales.

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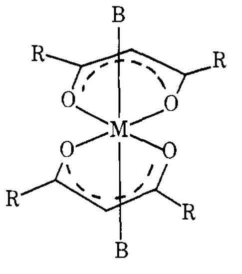
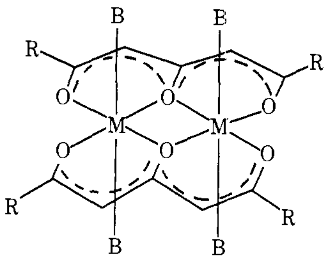
Copper(II), Nickel(II), and Cobalt(II) Chelates of 1,3,5,7-Tetraketonates. Characterization and Preliminary Magnetic Studies on Bi- and Trinuclear Chelates

Sir:

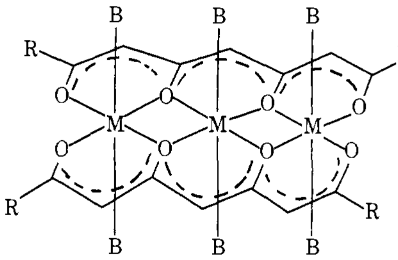
In the study of magnetic exchange phenomena in polynuclear metal clusters it would be desirable to be able to investigate homologous series of complexes in which the members of the series contain one, two, three, etc., metal ions. If the metal ions in each member of these series were in similar chemical environments, then the effect of exchange over varying numbers of metal centers could be critically assessed. A class of ligands we call the polyketones is capable of producing series of this type. The generalized structure for the first three members is shown below. In the series shown M is a divalent metal ion and B is a neutral ligand such as H_2O or pyridine. When M is Cu(II), the adduct ligands may or may not be present. However, when present no more than one per Cu(II) is normally found.



1,3-diketonates



1,3,5-triketonates



1,3,5,7-tetraketonates

The first member, the 1,3-diketonates, needs no further comment here. The second member, the 1,3,5-triketonates, has received very little attention. To date only dicopper(II) bis(1,3,5-triketonato) type complexes have been reported[1–3] although Ni(II),[4] Co(II),[5] Fe(II),[6] Mn(II),[6] and Cr(III)[6] chelates have been prepared and their magnetic properties studied in a preliminary manner. To our knowledge, no examples of the third member of the series, the 1,3,5,7-tetraketonates, have been reported. We wish to report at this time the first chelates of this type.

The tetraketonate complexes prepared contain the ligand 1,7-diphenyl-1,3,5,7-heptanetetraone. The ligand itself was first reported by Miles, Harris, and Hauser[7] who prepared it by the benzoylation of (1) acetylacetone and (2) 1-phenyl-1,3,5-hexanetrione. In our hands, method 2 was far more successful. Adopting the commonly used nomenclature of the 1,3-diketones, the trivial name for this ligand is dibenzoylacetylacetone. Henceforth, we will use the abbreviation H_3DBAA for the completely protonated molecule. The preparation of H_3DBAA involves a straightforward Claisen condensation using NaH as the base and monoglyme as the solvent. The golden, plate-like crystals melt at 91–93°. *Anal.* Calcd for $C_{19}H_{16}O_4$: C, 74.02; H, 5.22. Found: C, 74.15; H, 5.16. The molecule contains three enolizable protons and may function as a mono-, di-, or trianionic ligand, H_2DBBA^-, $HDBAA^{2-}$, and $DBAA^{3-}$.

Chelates were prepared in a variety of ways. The most successful methods used a 1.0:0.67 molar ratio of metal ion to H_3DBAA in MeOH–H_2O or acetone–H_2O solvent systems. Either NaOH or $NaC_2H_3O_2$ was added as a base. All of the chelates precipitated as powders that are relatively insoluble in common organic solvents and H_2O. They are soluble in coordinating solvents such as pyridine. Isolation of complexes with two or three metal ions appears to depend upon preparative details such as the solvent, temperature, and base used. The chelates were washed with H_2O, and for Ni(II) and Cu(II) complexes with dilute

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