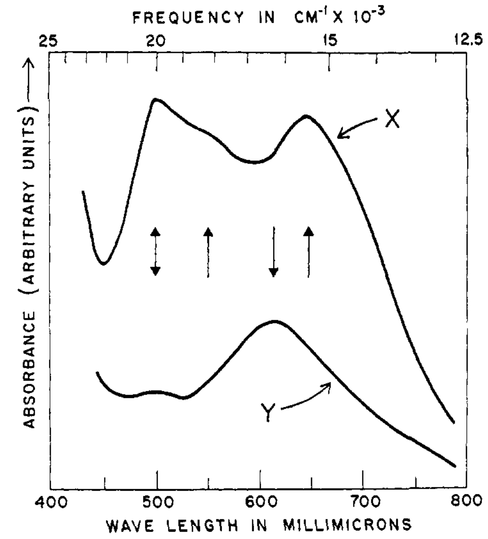

Figure 1. Spectra polarized along the x and y molecular axes for $Cu(DPM)_2$.

available as a suitable host for studies of the esr spectra of magnetically dilute $Cu(DPM)_2$. The investigation involved four phases:[15] (1) an LCAO-MO calculation[16] using the extended Hückel method and the Wolfsberg–Helmholz approximation, but with constraints imposed by the requirement that the coefficients of the d orbitals in the MO eigenvectors remain closely consistent with the magnitudes indicated for them by esr data; (2) a single crystal esr study to obtain accurate g values; (3) a study of the energies and polarizations of the visible "d–d" absorption bands; (4) a study of the near-ultraviolet (200–400 mμ) spectra and a partial reinterpretation[11,12] thereof, guided by the results of the MO calculations.

The MO calculation led to the general result, which did not change over considerable variations of the disposable parameters (*e.g.*, the Wolfsberg–Helmholz factor, the energies of Cu and O atomic orbitals) within reasonable ranges, that the d_{xy} orbital[17] lies some 18,000 cm^{-1} higher than the other four d orbitals, all of which lie within a few thousand wavenumbers of one another. This would suggest that the incompletely resolved absorptions observed for $Cu(DPM)_2$ and $Cu(acac)_2$ in the region 15,000–20,000 cm^{-1} include all four "d–d" transitions, in agreement with the views of some previous workers, but contrary to those of others who have suggested that only three "d–d" bands were to be found in this region, the fourth being identified as a shoulder at ~ 26,000 cm^{-1}.

This conclusion is in good accord with the esr results. The observed g values (g_z = 2.244, $g_x = g_y$ = 2.051) are nearly the same as those[7] for $Cu(AcAc)_2$ (g_z = 2.264, $g_x = g_y$ = 2.053), and in both cases, using the appropriate molecular orbital coefficients, these data lead to the result that the $x^2 - y^2$, xz, and yz orbitals should lie within a range of ~5000 cm^{-1}.

Conclusive evidence that d_{z^2} also lies in this range, as indicated by the MO calculation, is provided by the polarized spectra, measured at 25°. Figure 1 shows the absorption of light polarized in the directions of the x and y molecular axes;[15] it was constructed from the results of polarization measurements made on the 001, 100, and 110 faces of crystalline $Cu(DPM)_2$. None of the absorption in the range 450–800 mμ had principally z polarization; thus the absorption is all in-plane polarized. It is evident from Figure 1 that the visible absorption of $Cu(DPM)_2$ consists of *four* overlapping bands, whose maxima occur at ~20,000, ~18,200, ~16,400, and ~15,600 cm^{-1}.

Finally, it may be noted that the assignment of the near-ultraviolet spectrum, which consists of three distinct maxima, at 48,600, 40,000, and ~33,500 (doublet) as well as a shoulder at ~26,000 cm^{-1}, has been reconsidered on the basis of the results of the MO calculation and some rough indications of polarizations obtained using hopper crystals. The doublet around 33,500 cm^{-1} is again assigned as two close π–π^* transitions, in agreement with the conclusions of nearly all previous workers. The band at 40,000 cm^{-1} appears most likely to be due to a transition from a ligand σ orbital to the d_{xy} orbital, as previously proposed.[11] The band at 48,600 cm^{-1}, for which a π–π^* assignment had previously been proposed by some[11,12] but rejected by other workers,[18] is now assigned as a d_{yz} to π^* band. The 26,000-cm^{-1} absorption is attributed to another ligand σ to d_{xy} transition.

Acknowledgment. All of the work summarized here will be published in detail in due course. We thank P. Ros, C. B. Harris, R. Hoffmann, E. Hazen, and D. Thompson for their help with some parts of the work, the U. S. Atomic Energy Commission for financial support, and the Socony Mobil Oil Company for a fellowship to J. J. Wise.

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(15) Molecular Cartesian axes are defined throughout so that z is perpendicular to the molecular plane, x bisects O–Cu–O angles within the chelate rings, and y bisects O–Cu–O angles between different chelate rings. The molecular symmetry is D_{2h}.

(16) With the collaboration of Dr. C. B. Harris.

(17) The designations "d_{ij}" or "d orbital" are used here for brevity to denote molecular orbitals of which the indicated Cu d orbital constitutes the major part.

(18) L. S. Forster, *J. Am. Chem. Soc.*, **86**, 3001 (1964).

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Organic Syntheses by Means of Noble Metal Compounds. XXVII.[1] Decarbonylation of Acyl Halides Catalyzed by a Rhodium Complex and Preparation of Acylrhodium Complexes by a Novel Addition Reaction of Acyl Halides

Sir:

We have reported that aldehydes can be decarbonylated smoothly at room temperature by the reaction with chlorotris(triphenylphosphine)rhodium.[2] The decarbonylation of acyl halides with the same complex again gives smooth decarbonylation under mild conditions to yield olefins, hydrogen chloride, and chlorocarbonylbis(triphenylphosphine)rhodium. When it was impossible to form olefins, alkyl or aryl chloride was the product. Thus this reaction is a very efficient and

$$RCH_2CH_2COCl + RhCl(Ph_3P)_3 \longrightarrow RCH{=}CH_2 + HCl + RhClCO(Ph_3P)_2$$

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(1) Part XXVI: J. Tsuji and N. Iwamoto, in preparation.

(2) J. Tsuji and K. Ohno, *Tetrahedron Letters*, No. **44**, 3969 (1965).

Table I. Decarbonylation of Acyl Chlorides

			Reaction		Products (%)	
Acyl chloride (g)	RhCl-(Ph$_3$P)$_3$, g	Solvent (ml)	Temp	Time	Olefin,[a] chloride	RhCCOl-(Ph$_3$P)$_2$
PhCH$_2$COCl (0.5)	0.462	Benzene (10)	Reflux	10 min	PhCH$_2$Cl (81)	(97)
PhCH$_2$COCl (0.5)	0.462	CH$_2$Cl$_2$ (10)	Room temp	1 days	PhCH$_2$Cl (86)	(95)
PhCH$_2$CH$_2$COCl (0.5)	0.462	Toluene (10)	Reflux	30 min	PhCH=CH$_2$ (71)	(80)

[a] The yield was determined by gas chromatography.

Table II. RCORhCl$_2$(Ph$_3$P)$_2$ Complex

				Anal, %							
		Mol wt		C		H		Cl		P	
R	Mp dec, °C	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
CH$_3$(CH$_2$)$_4$	173–177	724	797	63.21	63.16	5.15	5.14	9.03	8.91	7.74	7.78
CH$_3$(CH$_2$)$_5$	165–166	806	811	63.37	63.6	5.22	5.31	9.37	8.75	7.1	7.52
CH$_3$(CH$_2$)$_{14}$	135–137	904	937	66.37	66.59	6.58	6.51	7.63	7.58	6.87	6.61
Cyclohexyl	167–169	...	...	64.57	63.90	5.15	5.25	8.31	8.79		

specific method of decarbonylation of acyl halides under mild conditions and seems to be useful in organic syntheses. Some experimental results are shown in Table I.

By careful investigation of the reaction between acyl halide and chlorotris(triphenylphosphine)rhodium, we have found that a new acylrhodium complex can be isolated in a good yield with elimination of 1 mole of triphenylphosphine under carefully controlled conditions.[3] Oxidative addition of acyl chloride to form a five-coordinated rhodium acyl complex appears to occur.

$$\mathrm{RCOCl + RhCl(Ph_3P)_3 \longrightarrow RCORhCl_2(Ph_3P)_2 + Ph_3P}$$

A number of complexes having acyl–metal bonds are known and are usually prepared by insertion of carbon monoxide into an alkyl–metal bond. Although the addition of covalent compounds to coordinately unsaturated metal compounds is a common reaction, this is the first example that an acyl complex is formed by the oxidative addition of acyl halide to a complex. Also this result indicates that an electrophilic attack on the rhodium by the carbonyl carbon is possible.

The following is a typical example. Chlorotris(triphenylphosphine)rhodium (9.24 g, 0.01 mole) was dissolved in anhydrous benzene (30 ml) and palmitoyl chloride (R = CH$_3$(CH$_2$)$_{14}$; 3.02 g, 0.11 mole) was added under nitrogen. The mixture was refluxed for 20 min in an oil bath. The dark red color of the original mixture instantly turned orange-red. Most of the benzene was removed and hexane was added to the residue to give a pale brown solid (9.20 g, 99%). The solid was dissolved in benzene and reprecipitated with ethanol to give dichloropalmitoylbis(triphenylphosphine)rhodium. The complex showed a sharp infrared band at 1715 cm^{-1} (acylrhodium carbonyl). The nmr spectrum showed a triplet at τ 7.08 (two protons, methylene protons next to the carbonyl). The following other peaks are consistent with the assigned structure: τ 2.34 (12 H), 2.58 (18 H), 8.69 (26 H), 9.09 (3 H). The complex is stable in air and does not react with water and alcohols.

Other acyl chlorides formed the corresponding complexes, but the stability of the complexes is somewhat different depending on the structure of acyl chloride. Some complexes obtained are shown in Table II. Acetyl chloride and benzoyl chloride were exceptions. They gave CH$_3$RhCOCl$_2$(Ph$_3$P)$_2$ and PhRhCOCl$_2$(Ph$_3$P)$_2$, respectively, as reported by Wilkinson, *et al.*[3]

As expected, the complex gave rise to olefin, hydrogen chloride, and chlorocarbonylbis(triphenylphosphine)rhodium when heated. For example, the palmitoyl complex gave rise to *trans*-2-pentadecene, containing a small amount of isomeric pentadecenes. However, 1-pentadecene was selectively obtained when the complex was treated with an equivalent amount of iodine in chloroform at room temperature. By the reaction of carbon monoxide (50 kg/cm^2) at room temperature with the acyl complex, the acyl chloride was recovered in a high yield.

The above results, combined with the Wilkinson's works, give very important clues to the mechanism of carbonylation and decarbonylation reactions catalyzed by noble metal compounds, which we will discuss elsewhere.

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[3] Recently, Wilkinson, *et al.*, reported the formation of an acylrhodium complex by carbonylating the ethylrhodium complex, without giving experimental details: M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 129 (1966).

Bullvalene. Motion in the Solid

Sir:

Since the synthesis of bullvalene by Schröder and the confirmation[1] of the prediction by Doering and Roth[2] that at high temperatures the nmr spectrum in solution would consist of a single line, there has been much interest in organic molecules with fluctuating structures. Saunders[3] has measured the rate of rearrangement in bullvalene as a function of temperature by nmr as has Gutowsky[4] using a spin-echo nmr technique. The activation parameters which were determined in these two solution investigations are in agreement.

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(1) G. Schröder, *Angew. Chem.*, **75**, 722 (1963).

(2) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(3) M. Saunders, *Tetrahedron Letters*, 1699 (1963).

(4) A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc.*, **87**, 4092 (1965).