cyanate derivatives. For example, the use of absolute ethanol as a solvent for phenyl azide gave good yields of phenylurethan.

It is tempting to speculate that the reaction proceeds by thermal decomposition of the azide to the nitrene which then reacts as shown: $C_6H_5N_3 \rightarrow C_6H_5N + N_2$, $C_6H_5N + CO \rightarrow C_6H_5NCO$. The reaction of 2-azidobiphenyl with CO resulted in some 2-isocyanatobiphenyl (10%), although the major product was carbazole (85%). The ring closure to carbazole has previously been used by Smith[10] and others[2] as evidence for nitrene intermediates.

Further work to elucidate the mechanism of this new route to isocyanates and isocyanate derivatives is currently in progress in this laboratory.

(10) P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, **84**, 480 (1962).

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Transition Metal π Complexes of Phosphine

Sir:

We wish to report some results of a comprehensive investigation of the field of transition metal π complexes of phosphine[1-4] which presage a substantial scope and a diversity for this area of chemistry.

Air-stable and sublimable bis(phosphine)metal tetracarbonyls of chromium, molybdenum, and tungsten have been prepared by a ligand displacement reaction with the recently described octahydrotriborotetracarbonyl metalate anions.[5]

$$(OC)_4MB_3H_8^- + 2PH_3 \xrightarrow{\text{THF}} (OC)_4M(PH_3)_2 + B_3H_8^- \qquad (1)$$

The colorless to faintly yellowish, crystalline $(OC)_4M(PH_3)_2$ complexes have been characterized by elemental,[6] spectroscopic, and mass spectrometric analyses. The infrared spectra (KBr disk) show only minor individual differences among the three metal derivatives. The pertinent features are a sharp P–H stretching vibration[7] at 2400 cm^{-1} and two strong P–H bending modes at 1015 and 1000 cm^{-1}. Consistent with C_{2v} symmetry in a *cis* configuration, there are four carbonyl-stretching bands, *e.g.*, 2082, 2038, 1940, and 1930 cm^{-1} for $(OC)_4W(PH_3)_2$. The carbonyl frequencies are shifted to higher wave numbers than in *cis*-$[(C_6H_5)_3P]_2W(CO_4)$[8] which is provisionally taken as evidence for strong π-acceptor behavior of PH_3 in these complexes. The mass spectrum showed parent peaks at the expected positions and other major peaks corresponding to the fragment ions $M(CO)_3P_2^+$, $M(CO)_3P^+$, $M(CO)_2P^+$, $M(CO)P^+$, MP^+, and M^+.

The H^1 and P^{31} nmr chemical shift and coupling data for the molybdenum and tungsten derivatives, respectively, are τ 6.31 and 5.98, J_{P-H} = 324 and 338 cps, and δ +155 and +175 ppm (external H_3PO_4 reference). The coordination chemical shift, defined as $\delta_{\text{complex}} - \delta_{\text{free ligand}}$, is −83 ppm for $(OC)_4Mo(PH_3)_2$ and −63 ppm for $(OC)_4W(PH_3)_2$ and, while the absolute values are higher by about 20 ppm than those reported[9] for complexes of substituted phosphines, the difference between the molybdenum and tungsten compounds is of the same order of magnitude as reported earlier.[9]

A monophosphine derivative of manganese was obtained by reaction of phosphine with bromomanganese pentacarbonyl. The molecular $BrMn(CO)_4PH_3$ species sublimes at 80° (0.001 mm) with attendant decomposition. The P–H stretching vibrations are at 2410 and 2370 cm^{-1}. Mass spectral analysis shows a parent peak and then a fragmentation pattern consistent with consecutive loss of four carbonyl groups. The nmr parameters are τ 6.58 and J_{P-H} = 355 cps.

Other reactions leading to the formation of phosphine complexes are schematically outlined below.[10,11]

$$\begin{aligned}
PH_3 + [(C_6H_5)_3P]_2PdCl_2 &\longrightarrow \{[(C_6H_5)_3P](PH_3)PdCl\}_4 \\
[(C_6H_5)_3P]_2PtI_2 &\longrightarrow Pt_3[P(C_6H_5)_3]_3(PH_3)_3I_2 \\
Ru(CO)_2Cl_2 &\longrightarrow Ru_3(CO)_8(PH_3)_4 \\
Rh_2(CO)_4Cl_2 &\longrightarrow Rh_6(CO)_8(PH_3)_8 \\
Ni(C_5H_5)_2 &\longrightarrow Ni(C_5H_5)_2(PH_3)_2 \\
[(C_6H_5)_3P]_3RhCl &\longrightarrow [(C_6H_5)_3P]_2Rh(PH_3)Cl \\
[(C_6H_5)_3P]_2Ir(CO)Cl &\longrightarrow [(C_6H_5)_3P](PH_3)Ir(CO)Cl
\end{aligned}$$

The most striking phenomenon in phosphine chemistry appears to be the facile generation of metal clusters from relatively simple starting materials. A rigorous physical characterization of some of these clusters has been impeded by their relative intractability, and the possibility of PH_2 bridging groups must be considered. Hence, at this time the formulation of the black, insol-

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(1) A few adducts of metal halides with PH_3 are reported in the older literature. Examples are $TiX_4 \cdot PH_3$ and $TiX_4 \cdot 2PH_3$ (X = Cl, Br)[2] and $CuCl \cdot PH_3$, $CuI \cdot 2PH_3$, and $2AgI \cdot PH_3$.[3] These thermally unstable compounds readily lose PH_3, usually below room temperature, and are therefore best defined as σ-type adducts with minimal strengthening of the metal–phosphorus bond by π-type overlap. The photochemical preparation of π-$C_5H_5V(CO)_3PH_3$ has just recently been described,[4] and other PH_3 monosubstitution products of transition metal carbonyls have been mentioned in a footnote of the latter communication.

(2) R. Höltje, *Z. Anorg. Allegem. Chem.*, **190**, 241 (1930).

(3) R. Scholder and K. Pattock, *ibid.*, **220**, 250 (1934).

(4) E. O. Fischer, E. Louis, and R. J. J. Schneider, *Angew. Chem.*, **80**, 122 (1968).

(5) (a) F. Klanberg and L. J. Guggenberger, *Chem. Commun.*, 1293 (1967). (b) Reaction 1 appears to be generally applicable for the preparation of *cis*-$L_2M(CO)_4$ compounds. The difficultly accessible bis(isonitrile) and bis(triphenylphosphine) derivatives have been obtained in practically quantitative yield by this method.

(6) A sample analysis for $(OC)_4Mo(PH_3)_2$ is: Calcd: C, 17.4; H, 2.2; O, 23.3; P, 22.5; Mo, 34.8. Found: C, 17.2; H, 2.2; O, 23.2; P, 22.3; Mo, 34.3.

(7) This absorption band may consist of two unresolved components. In solution it is broadened and shifted to 2355 cm^{-1}.

(8) Found:[5b] 2022, 1923, 1894, and 1880 cm^{-1}.

(9) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Am. Chem. Soc.*, **89**, 5573 (1967).

(10) Correct elemental analyses were obtained for all of the compounds.

(11) Preparation of the complexes comprises introduction of phosphine into a solution or suspension of the indicated starting material in a common organic solvent at temperatures between 25 and 80°. In the case of the nickelocene derivative, the best synthetic procedure is the direct interaction of the reagents in a sealed tube at about 10 atm.

uble rhodium cluster as $Rh_6(CO)_8(PH_3)_8$ is based on compositional analysis and analogy to the known polynuclear $Rh_6(CO)_{16}$ molecule. Molecular weight studies indicate that the palladium and platinum clusters are tetramers and trimers, respectively. A possible structure for the deep red, diamagnetic palladium cluster is a tetrahedron of palladium atoms with the tetrahedral faces bridged by chlorine atoms and with triphenylphosphine and phosphine terminally bonded to palladium. The platinum core cluster may be analogous to $(C_8H_{12})_3Pt_3(SnCl_3)_2$[12] with a triangular array of platinum atoms bridged by iodine atoms above and below the plane. In the rhodium complex $[(C_6H_5)_3P]_2Rh(PH_3)Cl$, obtained in near-colorless needles, there are rather curious infrared characteristics. There is a band at 2350 cm^{-1} which must be assigned to a P–H stretching frequency as well as a very sharp band at 2150 cm^{-1} which must be due primarily to a Rh–H vibration. The molecularity of this particular species has not been determined, but the presence of the band at 2150 cm^{-1} connotes interaction between one of the ligand–hydrogen atoms and the metal atom or that hydrogen abstraction has occurred to give a rhodium(III) species.

A comprehensive account of this new area of chemistry as well as structural details will be published shortly.

[12] L. J. Guggenberger, *Chem. Commun.*, in press.

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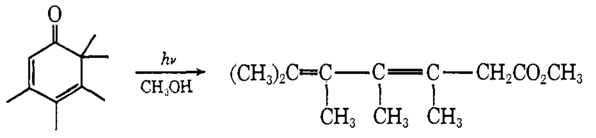
On the Mechanism of 2,4-Cyclohexadienone Photoisomerization

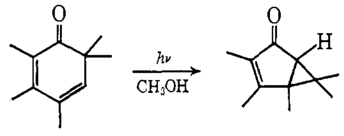
Sir:

Most 2,4-cyclohexadienones undergo reversible ring fission on irradiation to form ketenes which may be trapped by suitable nucleophiles.[1,2,2a] On the other hand certain alkyl-substituted dienones undergo specific photoisomerization to bicyclo[3.1.0]hexenones to the complete exclusion of ring-opened products, even with alcohols as solvent.[3] An important controlling factor in these processes is the pattern of substitution in the dienone, and it has been shown that relatively subtle structural changes have a pronounced effect in determining which of these two reactions is observed.[4] For example, the pentamethyldienones 1 and 2 give only the products shown on irradiation under identical conditions.[4]



$$(CH_3)_2C{=}\underset{CH_3}{C}{-}\underset{CH_3}{C}{=}\underset{CH_3}{C}{-}CH_2CO_2CH_3$$

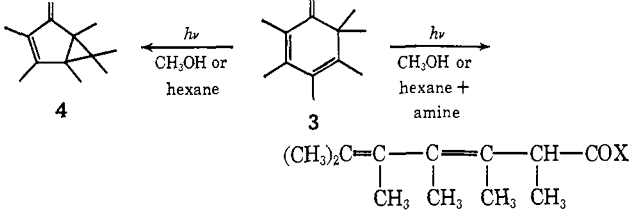
1



2

In this communication we wish to present evidence that, *in all these cases, the only photochemical reaction is ring opening to a ketene; all other processes, including isomerization to a bicyclo[3.1.0]hexenone, are thermal.*

Irradiation of dienone 3 in alcohol or hexane gives only ketone 4. We have now observed that incorporation of dimethylamine in the solvent leads to the photochemical formation of amide 5a in high yield (92% in hexane).[5] Similar irradiation of 3 in hexane containing cyclohexylamine gave (93% yield) crystalline amide 5b, mp 80–80.5°.[6]



4 3

$$(CH_3)_2C{=}\underset{CH_3}{C}{-}\underset{CH_3}{C}{=}\underset{CH_3}{C}{-}\underset{CH_3}{CH}{-}COX$$

5a, X = $N(CH_3)_2$
b, X = NH-cyclohexyl

The possibility that a ketene might be a common intermediate in both reactions was confirmed by low-temperature studies. A solution of 3 in methyltetrahydrofuran was irradiated at −100° in a sodium chloride cavity cell, and the course of the reaction was followed by ir spectroscopy. After 20-min exposure the dienone maxima at 1570, 1630, and 1640 cm^{-1} were completely replaced by a single intense absorption at 2100 cm^{-1}, attributable to ketene 6. When the solution was warmed to room temperature, the ketene absorption band disappeared and was replaced by the original dienone maxima plus a weak band at 1685 cm^{-1} due to a small amount of the ketone 4. When ethanol was injected into a similar ketene solution at −100° the maxima at 2100 cm^{-1} immediately disappeared, and intense bands due to ketone 4 appeared, together with bands due to a smaller amount of dienone 3. Thus the ketene may cyclize thermally to either the starting material or to the ketone 4; indeed, the ketene could not be induced to form 4 photochemically. Cyclization to 4 is favored by the presence of ethanol which, notably, does not react with the ketene to give ester.

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[1] (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960); (b) for a review, see G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, 4, 211 (1965); (c) P. M. Collins and H. Hart, *J. Chem. Soc., C*, 1197 (1967).

[2] A ketene intermediate has been detected by ir spectroscopy at low temperatures (G. Quinkert, private communication).

[2a] Note Added in Proof. After this paper was submitted, ketene detection was also reported by O. L. Chapman and J. D. Lassila, *J. Am. Chem. Soc.*, 90, 2449 (1968).

[3] H. Hart, P. M. Collins, and A. J. Waring, *ibid.*, 88, 1005 (1966).

[4] P. M. Collins and H. Hart, *J. Chem. Soc., C*, 895 (1967).

[5] The structure was deduced from elemental analysis and spectra. Consideration of the nmr spectrum of the amide derived from 3-4-CD_3 eliminated alternative structures which might have arisen from 1,4 or 1,6 addition of amine to the intermediate ketene.

[6] This amide seems to be a single isomer, whereas amide 5a was a mixture of geometric isomers. The reason for this difference remains to be elucidated.