nuclei in the ffars compound. This could be caused by a decrease in 4s population, or by an increase in 3d density which would shield the nucleus from the 4s electrons. The former would imply that a CO group is a slightly more efficient σ donor than the $AsMe_2$ group.

The alternative explanation, an augmented 3d electron density, could arise from three possible effects: (1) an increase in σ donation of $As(CH_3)_2$ relative to CO which would then increase the 3d character; (2) an increase in ligand-to-metal π donation; (3) a decrease in metal-to-ligand back π donation. It seems likely that the direct 4s term is greater than the direct 3d term, in which case an increase in σ donation would cause a negative rather than positive change in the isomer shift. Both the other possible explanations would yield positive shifts.

The larger electric field gradient at the equivalent iron nuclei in the ffars compound may arise both from π delocalization in the cyclobutene ring and from the fact that the ligand lies in the plane of the iron atoms. The splittings for $Fe_3(CO)_{12}$ and $ffarsFe_3(CO)_{10}$ show a stronger temperature dependence than most d^{10} iron complexes. This may be due to the bridging carbonyls and merits further study as it implies the existence of a fairly low-lying electronic excited state in these compounds.

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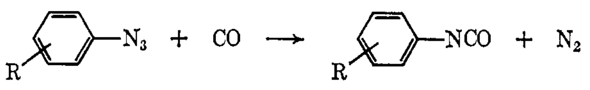
The Reaction of Organic Azides with Carbon Monoxide. A New Route to Isocyanates

Sir:

In the course of our work on new routes to isocyanates[1] we became interested in the reactions of nitrene intermediates. Investigations of nitrene intermediates have generated numerous publications in recent years.[2] In view of the similarity of nitrene reactions to those of carbenes, it was decided to investigate whether organic azides react with carbon monoxide to produce isocyanates.



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It is known[3] that methylene formed from the photochemical decomposition of ketene will react with CO to re-form ketone. Also, diazomethane has been decomposed in CO to produce ketene.[4] In addition, isocyanic acid has previously been found[5] as a product of the thermal decomposition of chloramine in CO. Chambers[6] and coworkers have reported that hexafluoroazomethane reacted with CO at 325° and 650 atm to give an 88% conversion to trifluoromethyl isocyanate. These authors postulated a nitrene intermediate which reacts with the CO. Most recently Collman and coworkers[7] have treated phenyl azide and acid azides with *trans*-chlorocarbonylbis(triphenylphosphine)iridium to form isocyanate products. Collman states,[8] however: "In the absence of a metal complex, CO and organic azides do not react at a measurable rate." We now report the first direct synthesis of free isocyanates from aromatic azides and uncomplexed CO in an uncatalyzed reaction.

Attempts to pyrolyze phenyl azide in a CO stream at atmospheric or reduced pressure resulted in only azobenzene and tar. However, when phenyl azide was thermally decomposed in an autoclave under sufficient CO pressure, phenyl isocyanate was obtained as the only product of the reaction. Benzene and 1,1,2-trichloro-1,2,2-trifluoroethane have been used as solvents. A pressure dependence has been noted for the reaction: at 37 atm equal amounts of phenyl isocyanate and azobenzene were obtained, at 136 atm the product was phenyl isocyanate with only a trace of azobenzene, and above this pressure only phenyl isocyanate was detected.

Examples of other azides which have been successfully converted to the corresponding isocyanates include **1** where R = o-CH_3, o-C_6H_5, p-CH_3, p-NO_2, p-OCH_3, and p-Cl. Ethyl azidoformate in benzene or cyclohexane appeared to yield products of reaction with the solvents. In trichlorotrifluoroethane, however, carbethoxy isocyanate was isolated [bp 25° (10 mm); 32% yield; ν_{NCO} 2230 cm^{-1}; N-carbethoxyurethan, mp 48–49° (lit.[9] mp 49–50°)].

The reactions have been run in stainless-steel, tantalum-lined and glass-lined autoclaves. Reaction times have varied from 15 to 90 min at 160–180°. To ensure complete conversion to isocyanate we have generally worked at pressures between 200 and 300 atm. A sample procedure is as follows. To a 250-ml, glass-lined autoclave was added 11.9 g (0.1 mol) of phenyl azide and 100 ml of 1,1,2-trichloro-1,2,2-trifluoroethane. The autoclave was flushed once with CO and then pressurized with CO (Air Products and Chemicals, Inc., CP grade) to 300 atm. The reaction mixture was heated with rocking at 180° for 1.5 hr. After cooling, the autoclave was discharged under N_2. The presence of phenyl isocyanate was shown by ir and vpc examination (100% conversion) with no indication of any other products. Vacuum fractional distillation yielded pure phenyl isocyanate, bp 50° (10 mm) (5.6 g, 47% yield). An additional 3.6 g of diphenylurea (presumably from moisture) was also obtained for a material balance of 80%.

This procedure gives a general method for making isocyanates from readily available azides. The reaction can be carried out in reactive solvents to yield iso-

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[1] W. B. Hardy and R. P. Bennett, *Tetrahedron Letters*, 961 (1967); R. P. Bennett, W. B. Hardy, R. K. Madison, and S. M. Davis, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. O-89.

[2] See, for example, L. Horner and A. Christmann, *Angew. Chem. Intern. Ed. Engl.*, 2, 599 (1963); R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

[3] G. B. Kistiakowsky and W. L. Marshall, *J. Am. Chem. Soc.*, 74, 88 (1952); T. B. Wilson and G. B. Kistiakowsky, *ibid.*, **80**, 2934 (1958).

[4] H. Staudinger and O. Kupfer, *Ber.*, **45**, 508 (1912).

[5] J. Jander and J. Fischer, *Z. Anorg. Allgem. Chem.*, **313**, 37 (1961).

[6] W. J. Chambers, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 2337 (1962).

[7] J. P. Collman, M. Kubota, J-Y. Sun, and F. Vastine, *ibid.*, **89**, 169 (1967).

[8] J. P. Collman, M. Kubota, and J. W. Hosking, *ibid.*, **89**, 4809 (1967).

[9] L. G. R. Tompkins and E. F. Degering, *ibid.*, **69**, 2616 (1947).

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]

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

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.