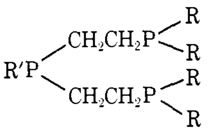
$CH_2P(C_6H_5)_2]_2$ (I: R = C_6H_5, R′ = CH_3), mp 74°. The completely methylated tri(tertiary phosphine) $CH_3P[CH_2CH_2P(CH_3)_2]_2$ (I: R = R′ = CH_3), bp 103° (0.03 mm), was prepared similarly from $(CH_3)_2PH$ and $CH_3P(S)(CH{=}CH_2)_2$ followed by $LiAlH_4$ reduction.



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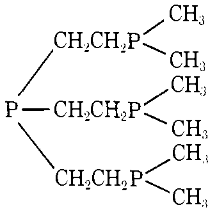

II

The completely methylated tripod tetra(tertiary phosphine) $P[CH_2CH_2P(CH_3)_2]_3$ (II) was prepared by a related method. Addition of 3 equiv of $(CH_3)_2PH$ (from tetramethyldiphosphine disulfide and $LiAlH_4$[3]) to trivinylphosphine sulfide under the usual conditions gave a solid product which was desulfurized with $LiAlH_4$ in boiling dioxane to give a small quantity of colorless liquid $P[CH_2CH_2P(CH_3)_2]_3$ (II), bp ~125° (0.35 mm), which froze slightly below room temperature. This compound is of interest in being a potential tetradentate ligand with only aliphatic groups bonded to the phosphorus atoms.

The vinylphosphine sulfides needed for these syntheses are prepared by routine reactions of vinylmagnesium bromide with appropriate phosphorus halide derivatives. Thus, reaction of $(CH_3)_2P(S)Br$[4] with vinylmagnesium bromide gave an 80% yield of white crystalline sublimable $(CH_3)_2P(S)CH{=}CH_2$, mp 52–54°. Similar reactions of $CH_3P(S)Cl_2$ and $PSCl_3$ with vinylmagnesium bromide gave an 18% yield of liquid $CH_3P(S)(CH{=}CH_2)_2$, bp 88° (0.5 mm), and an 8% yield of liquid $SP(CH{=}CH_2)_3$, bp 85° (0.35 mm), respectively.

Investigations of the syntheses of more complex methylated poly(tertiary phosphines) by this method and studies on the transition metal complexes of methylated poly(tertiary phosphines) are currently in progress and will be reported in future publications.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-71-2000 and to the National Science Foundation for the support of one of us (P. K. H).

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[3] G. W. Parshall, *Inorg. Syn.*, **11**, 157 (1969).
[4] R. Schmutzler, *Inorg. Syn.*, **12**, 287 (1970).
[5] Postdoctoral research associate, 1971–1973.
[6] Undergraduate research participant, summer 1972.

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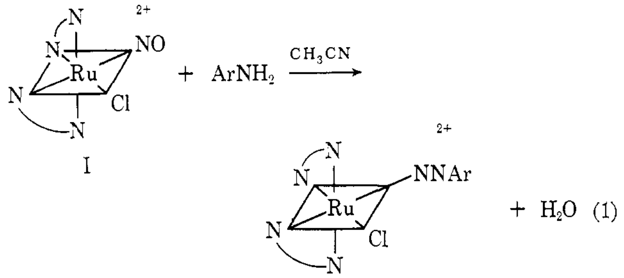
Diazonium Complexes of Transition Metals. Diazotization by Coordinated Nitrosyl

Sir:

We wish to report the generation of aryldiazonium ligands within the coordination sphere of ruthenium by reaction of aromatic amines with the nitrosyl group in $[Ru(bipy)_2(NO)Cl](PF_6)_2$ (I) (bipy is 2,2′-bipyridine). Although the reactions are novel, they were anticipated since the coordinated nitrosyl group in I has been shown to react chemically as NO^+.[1,2] *Anal.* Calcd for $[(bipy)_2ClRuN_2C_6H_4OCH_3](PF_6)_2$: C, 37.02; H, 2.63; N, 9.61. Found: C, 36.55; H, 2.60; N, 9.43. Calcd for $[(bipy)_2ClRuN_2C_6H_4CH_3](PF_6)_2$: C, 37.70; H, 2.68; N, 9.78; Cl, 4.18. Found: C, 37.66; H, 2.66; N, 9.64; Cl, 4.34.



IIa, Ar = p-$CH_3OC_6H_4$-
b, Ar = p-$CH_3C_6H_4$-

Direct reactions between aryldiazonium ions and transition metal complexes have led to the formation of arylazo complexes,[3–9] *ortho*-substituted phenylazo complexes,[10] and metallotetrazenes.[11] Most of the isolable arylazo complexes obtained with the metals Pt,[3,4,9] Mo,[5] Rh,[6,12] Ir,[7] Re,[8] Os,[12] and Ru[12] can be formulated as having coordinated $ArN{=}N^-$; they are characterized by ν_{NN} ranging from 1444 to 1642 cm^{-1}.[3–10,13] An X-ray crystallographic study on $ReCl_2(N_2C_6H_5)(P(CH_3)_2C_6H_5)_3$ has shown that the N=N–Ar bond angle is 118°, which is close to the 120° angle expected for sp^2 nitrogen.[8]

In contrast to the cases reported previously, the available chemical and physical evidence indicates that our compounds should be formulated as containing $ArN{\equiv}N^+$. Thus, it appears that the properties of bound ArN_2 can vary from arylazo (ArN_2^-) to diazonium (ArN_2^+), much as the properties of coordinated NO have been found to vary from NO^- to NO^+.[14]

Compounds IIa and IIb have N–N stretching frequencies at 2095 and 2080 cm^{-1} in acetonitrile solution, compared to ~2260 cm^{-1} for the uncomplexed tetrafluoroborate salts (KBr pellets). These values are the highest yet reported for the ArN_2 ligand by about 200 cm^{-1}. For comparison, the ν_{NO} values for $[Ru(bipy)_2(NO)Cl](PF_6)_2$ and $NO^+SbCl_6^-$ are 1932 (acetonitrile)

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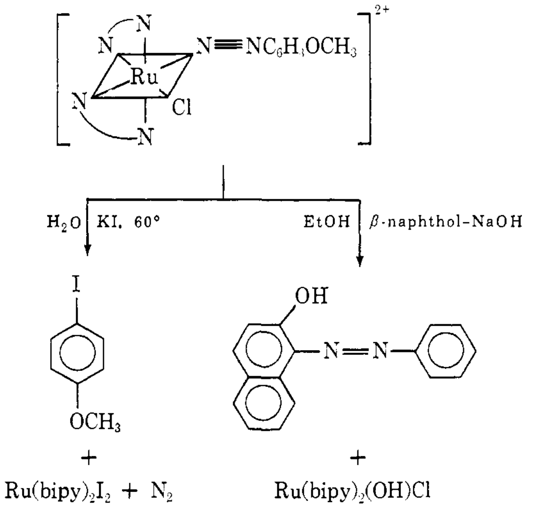
[1] T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Commun.*, 872 (1970); J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 2150 (1971).
[2] F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, **93**, 1294 (1971); S. A. Adeyemi, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, **11**, 994 (1972).
[3] G. W. Parshall, *J. Amer. Chem. Soc.*, **87**, 2133 (1965).
[4] G. W. Parshall, *J. Amer. Chem. Soc.*, **89**, 1822 (1967).
[5] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).
[6] M. C. Baird and C. Wilkinson, *J. Chem. Soc. A*, 865 (1967).
[7] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969).
[8] V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Commun.*, 1083 (1970).
[9] S. Cenini and R. Ugo, *J. Chem. Soc. A*, 3442 (1971).
[10] F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, **94**, 645 (1972).
[11] F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, **93**, 1826 (1971).
[12] K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 176 (1973).
[13] G. W. Rayner-Canham and D. Sutton, *Can. J. Chem.*, **49**, 3994 (1971).
[14] B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

and 2250 cm^{-1},[14] respectively. Compound IIa was shown to be a 2:1 electrolyte by a conductometric titration in acetone, as expected for a diazonium complex of ruthenium(II). Reaction 1 (Ar = p-$CH_3OC_6H_4$–) was also carried out using $Ru(bipy)_2(^{15}NO)Cl^{2+}$, and the diazonium product showed a $\Delta\nu_{NN}$ of *ca.* −30 cm^{-1} (acetonitrile). The observed shift in ν_{NN} shows that the nitrosyl nitrogen is incorporated into the product, probably still bound to the ruthenium. The importance of back-bonding in both the nitrosyl and diazonium complexes is clear from their electronic spectra. The spectra of bis-2,2′-bipyridyl complexes of ruthenium(II) are characterized by intense, low energy $t_{2g} \rightarrow \pi^*$(bipy) transitions (*e.g.*, λ_{max} 555 nm for $Ru(bipy)_2Cl_2$ in dichloromethane).[15,16] For the complexes $Ru(bipy)_2(NO)Cl^{2+}$ and $Ru(bipy)_2(N_2C_6H_4OCH_3)Cl^{2+}$ in acetonitrile, the first transitions are observed at λ_{max} 325 and λ_{max} 353 nm, respectively, indicating considerable stabilization of the t_{2g} levels by π bonding.

Recently, Laing, Robinson, and Uttley have reported the preparations of the complexes $MX_3(N_2Ar)(P(C_6H_5)_3)_2$ (M = Ru, Os; X = Cl, Br) by direct reaction between diazonium tetrafluoroborate salts and $MX_2(P(C_6H_5)_3)_3$ in the presence of LiX.[12] Their reported ν_{NN} values occur in the range 1850–1900 cm^{-1}, and from a preliminary X-ray study[12] the N–N–Ar angle in one of the ruthenium complexes was found to be 137°. This report raises the interesting possibility that a range of cases intermediate between $ArN{=}N^-$ and $ArN{\equiv}N^+$ may exist in which the N–N–Ar bond angle varies from ~120 to ~180° with corresponding changes in ν_{NN} and in chemical reactivity.

In addition to physical properties of bound ArN_2^+, compound IIa showed chemical reactivity characteristic of a diazonium ligand stabilized by complexation. At 60° in aqueous solution N_2 gas is evolved. With excess KI, p-iodoanisole was produced along with $Ru(bipy)_2I_2$ and N_2 (eq 2). Complex IIa also reacts with β-naphthol in alkaline ethanolic solution to produce the known azo coupling product. The reaction of $[Ru(bipy)_2(NO)Cl](PF_6)_2$ with other aryl amines and with aliphatic amines seems to be general and further reactions are currently under investigation.



(2)

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(15) G. M. Bryant and J. E. Fergusson, *Aust. J. Chem.*, **24**, 257 (1971); J. E. Fergusson and G. M. Harris, *J. Chem. Soc. A*, 1293 (1966).

(16) S. A. Adeyemi, J. N. Braddock, T. R. Weaver, and R. W. Callahan, unpublished results.

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A Chain Photoreaction of Sodium Borohydride with Halogenated Aromatic Hydrocarbons. Evidence for Initiation by Aryl Radicals

Sir:

We wish to report that the photoreduction of the chloro, bromo, and iodo derivatives of aromatic hydrocarbons by sodium borohydride in aqueous acetonitrile solution proceeds *via* a radical chain mechanism to give the hydrocarbon in virtually 100% yield and in a quantum yield often considerably in excess of unity.

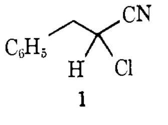
Continuing our studies[1] into the photoreduction of aromatics, we irradiated (λ 254 nm) solutions (0.5 *M*) of chloro-, bromo-, and iodobenzene with $NaBH_4$ (1.0 *M*) in 6% v/v aqueous acetonitrile. The sole organic product (glc) in all cases was benzene, formed in quantitative yield. The corresponding quantum yields[2] were 0.5, 5.7, and 7.5, respectively. In addition, (i) a gas was evolved shown to be mainly hydrogen with traces of diborane (*m/e* 28, 14), (ii) the solution contained halide ion, and (iii) a white solid was precipitated giving a positive test for borate. There was no detectable reaction with fluorobenzene.

To accommodate these results, we propose the mechanism shown in Scheme I.

Scheme I

$$\begin{aligned}
&C_6H_5{\cdot}X \xrightarrow{h\nu} [C_6H_5{\cdot}X]^* \longrightarrow C_6H_5{\cdot} + X{\cdot} && \text{initiation}\\
&X{\cdot} + BH_4^- \longrightarrow BH_3{\cdot}^- + X^- + H^+ &&\\
&\left.\begin{aligned}&C_6H_5{\cdot} + BH_4^- \longrightarrow BH_3{\cdot}^- + C_6H_5H\\ &C_6H_5X + BH_3{\cdot}^- \longrightarrow C_6H_5{\cdot} + BH_3 + X^-\end{aligned}\right\} && \text{propagation}\\
&2BH_3 \longrightarrow B_2H_6 \xrightarrow{H_2O} \text{borate} + H_2 &&\\
&C_6H_5{\cdot} + X{\cdot} \longrightarrow C_6H_5X && \text{termination}
\end{aligned}$$

The intervention of phenyl radicals was demonstrated (i) by showing that the photoreduction was totally inhibited by small amounts of acrylonitrile (an efficient trap for phenyl radicals) and (ii) by irradiating a mixture of chlorobenzene (0.5 *M*) and acrylonitrile (0.5 *M*) in acetonitrile, a procedure which gave rise to the products **1**, **2**, and **3**.



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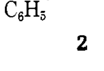

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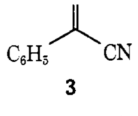

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It is known[3-5] that phenyl radicals generated by the

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(1) J. A. Barltrop, *Pure Appl. Chem.*, **33**, 179 (1973); J. A. Barltrop and R. J. Owers, *J. Chem. Soc., Chem. Commun.*, 592 (1972).

(2) These are initial values obtained by extrapolating quantum yields back to zero time.

(3) C. F. Koelsch, *J. Amer. Chem. Soc.*, **65**, 57 (1943).

(4) C. F. Koelsch and V. Boekelheide, *J. Amer. Chem. Soc.*, **66**, 412 (1944).

(5) J. K. Kochi, *J. Amer. Chem. Soc.*, **79**, 2942 (1957).