

the bicarbonato complexes reported here; none of them show an O–H stretching frequency in their ir spectra, and the hydrogen is also not observable by the nmr. However, it is not unlikely that the unobservable proton is involved in intra- and/or intermolecular hydrogen bonding, and precedents of analogous cases are known.¹⁴ The total properties of the key compound, $[\text{Rh}(\text{OCO}_2\text{H})(\text{CO})(\text{Ph}_3\text{P})_2]$ (**1a**), leave little doubt about its formula: (1) complete elemental analysis; (2) nonelectrolyte in $\text{C}_2\text{H}_5\text{OH}$; (3) diamagnetism and electronic spectrum (λ_{max} , 355 nm), both are typical of Rh(I);¹⁵ (4) formation, eq 3 and 4; and (5) expected reactions of a metal– OCO_2H group: (a) removal of the proton by base (**1a** \rightarrow **2a**), and (b) addition of proton by acids, followed by replacement of H_2CO_3 (**1a** \rightarrow **3a**, **4a**, **5a**).

The CO_2 fixation described here adds yet another mode of relatively few known carbon dioxide insertions into metal ligand or coordinated ligand bonds leading to isolable complexes: M–H, M–C, M–N, and MO_2 ¹⁶ and MOCH_3 .¹⁷ In the present instance, the principal questions are (a) whether the bond rupture involves the M–O or O–H linkage and (b) whether the initial attack of CO_2 occurs on the metal center or the coordinated OH. The latter appears to be the case with *six*-coordinated cobalt(III) (d^6),⁵ but here we deal with *four*-coordinated M(I) (d^8) complexes. It is hoped that planned mechanistic studies with labeled reactants will shed light on these problems.¹⁸

(14) (a) Solid KHCO_3 shows a weak ν_{OH} band at 2620 cm^{-1} .^{12a} (b) Internal hydrogen bonding has been observed between OCO_2 and H_2N in $[\text{Co}(\text{OCO}_2)(\text{NH}_3)]^+$, H. C. Freeman and G. Robinson, *J. Chem. Soc.*, 3195 (1965). (c) See ref 2.

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Sulfurization as a Means for the Protection of Trivalent Phosphorus Atoms in the Syntheses of Methylated Poly(tertiary phosphines)

Sir.

Numerous poly(tertiary phosphines) with $\text{PCH}_2\text{CH}_2\text{P}$ units have been synthesized by the base-catalyzed additions of phosphorus–hydrogen bonds to the vinyl double bonds in various vinylphosphine derivatives^{1,2} such as diphenylvinylphosphine and phenyldivinylphosphine. However, up to the present time this preparative method has been limited to the syntheses of poly(tertiary phosphines) with phenyl groups bonded to the positions of the trivalent phosphorus atoms not occupied by the CH_2CH_2 bridges. Extension of this preparative method to the syntheses of poly(tertiary phosphines) with methyl groups, rather than phenyl groups, bonded to the free positions of the trivalent

phosphorus atoms has been discouraged by the inconvenience of preparing and handling the very volatile and air-sensitive dimethylvinylphosphine and/or methyldivinylphosphine which would be required as starting materials. This communication reports a modification of this general preparative method which allows the syntheses of poly(tertiary phosphines) with $-\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ and $-\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)\text{CH}_2\text{CH}_2-$ units without the need to prepare and handle dimethylvinylphosphine and/or methyldivinylphosphine. The key feature of this new preparative method is the protection, as the corresponding phosphine sulfide, of the phosphorus atom(s) to which the methyl groups are bonded in the ultimate product. After the poly(tertiary phosphine) network is constructed by appropriate additions of phosphorus–hydrogen bonds to vinylphosphine sulfide derivatives, the protecting sulfur atom(s) are removed from the phosphine sulfide phosphorus atoms by treatment with lithium aluminum hydride in boiling dioxane to give the corresponding methylated poly(tertiary phosphine). The new methylated poly(tertiary phosphines) prepared by this method are of interest as potential ligands in coordination chemistry because they can act as multidentate ligands with very basic phosphorus donor atoms bearing methyl substituents. The partially sulfurized poly(tertiary phosphines) which are intermediates in this new synthetic method are also of interest in being readily accessible organophosphorus derivatives with phosphorus atoms in two different oxidation states.

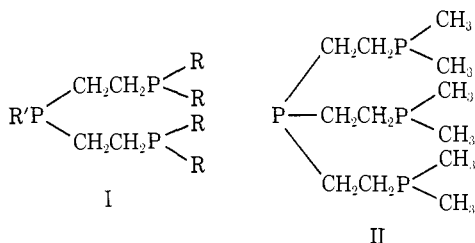
An example of the application of this new preparative procedure is the synthesis of the di(tertiary phosphine) $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$, which is the first example of a potentially chelating di(tertiary phosphine) with aryl groups on one phosphorus atom and alkyl groups on the other phosphorus atom. Treatment of a tetrahydrofuran solution containing equimolar quantities of $(\text{C}_6\text{H}_5)_2\text{PH}$ and $(\text{CH}_3)_2\text{P}(\text{S})\text{CH}=\text{CH}_2$ with a catalytic amount of potassium *tert*-butoxide gave, after an exothermic initial reaction and further heating at the boiling point for 26 hr, a 91% yield of the white crystalline diphosphine monosulfide $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{S})(\text{CH}_3)_2$, mp 130.5° . Desulfurization of this product with excess LiAlH_4 in boiling dioxane gave an 80% yield of the liquid ditertiary phosphine $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$, bp 160° (0.05 mm). This product and the other new compounds described in this paper were identified by correct analyses for three elements and consistent proton and phosphorus-31 nmr spectra.

Similar synthetic methods can be used to prepare various tri(tertiary phosphines) of the type $\text{R}'\text{P}(\text{CH}_2\text{CH}_2\text{PR}_2)_2$ (**I**). Thus addition of $\text{C}_6\text{H}_5\text{PH}_2$ to 2 equiv of $(\text{CH}_3)_2\text{P}(\text{S})\text{CH}=\text{CH}_2$ catalyzed by potassium *tert*-butoxide gave a 95% yield of the white crystalline triphosphine disulfide $\text{C}_6\text{H}_5\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{S})(\text{CH}_3)_2]_2$, mp 162° , which underwent desulfurization with excess LiAlH_4 in boiling dioxane to give an 80% yield of the liquid tri(tertiary phosphine) $\text{C}_6\text{H}_5\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]_2$ (**I**: $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_6\text{H}_5$), bp 147° (0.08 mm). Base-catalyzed addition of 2 equiv of $(\text{C}_6\text{H}_5)_2\text{PH}$ to $\text{CH}_3\text{P}(\text{S})(\text{CH}=\text{CH}_2)_2$ gave a 95% yield of the white crystalline triphosphine monosulfide $\text{CH}_3\text{P}(\text{S})[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$, mp $130\text{--}131^\circ$, which underwent desulfurization with LiAlH_4 in boiling dioxane to give a 57% yield of the white crystalline tri(tertiary phosphine) $\text{CH}_3\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$.

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$\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (I: $\text{R} = \text{C}_6\text{H}_5$, $\text{R}' = \text{CH}_3$), mp 74° . The completely methylated tri(tertiary phosphine) $\text{CH}_3\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]$ (I: $\text{R} = \text{R}' = \text{CH}_3$), bp 103° (0.03 mm), was prepared similarly from $(\text{CH}_3)_2\text{PH}$ and $\text{CH}_3\text{P}(\text{S})(\text{CH}=\text{CH}_2)_2$ followed by LiAlH_4 reduction.



The completely methylated tripod tetra(tertiary phosphine) $\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]_3$ (II) was prepared by a related method. Addition of 3 equiv of $(\text{CH}_3)_2\text{PH}$ (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 $\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2]_3$ (II), bp $\sim 125^\circ$ (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 $(\text{CH}_3)_2\text{P}(\text{S})\text{Br}$ ⁴ with vinylmagnesium bromide gave an 80% yield of white crystalline sublimable $(\text{CH}_3)_2\text{P}(\text{S})\text{CH}=\text{CH}_2$, mp $52\text{--}54^\circ$. Similar reactions of $\text{CH}_3\text{P}(\text{S})\text{Cl}_2$ and PSCl_3 with vinylmagnesium bromide gave an 18% yield of liquid $\text{CH}_3\text{P}(\text{S})(\text{CH}=\text{CH}_2)_2$, bp 88° (0.5 mm), and an 8% yield of liquid $\text{SP}(\text{CH}=\text{CH}_2)_3$, 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.

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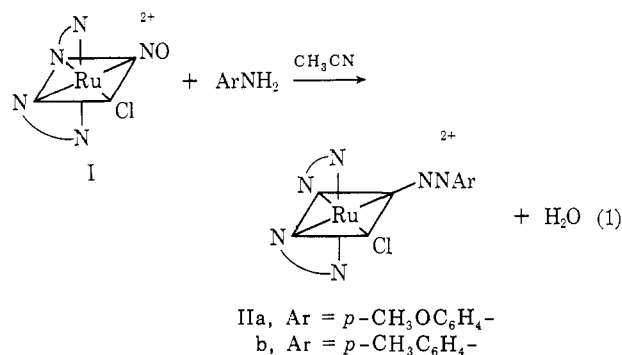
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Diazonium Complexes of Transition Metals.

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



$[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$ (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 $[(\text{bipy})_2\text{ClRuN}_2\text{C}_6\text{H}_4\text{OCH}_3](\text{PF}_6)_2$: C, 37.02; H, 2.63; N, 9.61. Found: C, 36.55; H, 2.60; N, 9.43. Calcd for $[(\text{bipy})_2\text{ClRuN}_2\text{C}_6\text{H}_4\text{CH}_3](\text{PF}_6)_2$: 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.

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 Ru¹² can be formulated as having coordinated $\text{ArN}=\text{N}^-$; they are characterized by $\nu_{\text{N-N}}$ ranging from 1444 to 1642 cm^{-1} .^{3-10,13} An X-ray crystallographic study on $\text{ReCl}_2(\text{N}_2\text{C}_6\text{H}_5)_2(\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5)_3$ has shown that the $\text{N}=\text{N}-\text{Ar}$ 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 $\text{ArN}=\text{N}^+$. 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 $\sim 2260 \text{ cm}^{-1}$ 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 $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$ and $\text{NO}^+\text{SbCl}_6^-$ are 1932 (acetonitrile)

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