is correct, then a study of the ^{13}CO species should lead to data in better agreement with the plastic cluster model.

The final question to be considered is whether a simple modification of the plastic cluster model enables a better fit to the data. We have considered several models of which we detail two as examples (Appendix). In one of these we introduce an interaction force constant between the long and short M–M bonds, and in the other we introduce it between the long bonds. As expected, the introduction of a further variable gives a better fit between the data and theory but the physical meaning of the improvement is unclear—thus, either of the two modifications enable the ratio of A_1 frequencies to be varied. Rather, we prefer to work with the simple plastic cluster model, for it predicts a frequency order that is in accord with all experimental data and gives predicted bond angles (using the expression for cos β given in the Appendix) that are in tolerable accord with the experimental values. Almost certainly a major error is the neglect of mixing of ν(M–M) with deformation modes, and this neglect is not adequately compensated by the introduction of ν(M–M) interaction constants in the simple model.

There remain two aspects of the vibrational spectra of $H_2Ru_4(CO)_{13}$ (Figure 3) that merit comment. First, it is the only species to show a strong Raman band that overlaps with the lower frequency end of the region assigned to δ(C–M–C)/δ(M–M–C), although the other compounds appear to have a similar band at much lower frequencies. It may be that this band is to be assigned to lattice translatory modes. Some of the translation vibrations of a cluster of isotropic, uncharged spherical molecules would be expected to show strong Raman activity because they correspond to changes in shape or orientation of the corporate polarizability ellipsoid. Such motions would normally be at low frequency (their acoustic counterparts have zero frequency at $k = 0$), but for rather irregular molecules supporting an inherent dipole, some considerably frequency increase is possible.

The second point worthy of comment is the rather broad infrared band centered at ~185 cm^{-1}, which is without counterpart in any of the other spectra. In that we are confident that it is not due to an impurity, we incline to assign it to δ(M–M–C) modes involving the bridge carbonyls, which must surely lie at a higher frequency than those of terminal carbonyl groups. If this assignment is correct, the absence of Raman activity on these vibrations is to be noted.

Experimental Section

$H_4Ru_4(CO)_{12}$[12] and $H_2Ru_4(CO)_{13}$[13] were prepared according to the literature methods. $H_4Os_4(CO)_{12}$ was kindly supplied by Dr. B. F. G. Johnson (Cambridge).

The Raman spectra were recorded on a Spex Raman spectrophotometer, Model 1401, equipped with a Spectra Physics Model 165 mixed-gas laser (exciting line 6471 Å) with incident power of ~25 mW. Very slow scanning enabled a resolution of ~4 cm^{-1}. The IR spectra in the 400–20 cm^{-1} region were obtained by a Beckman RIIC IR720M interferometer, the samples being dispersed in pressed polyethene plates.

Acknowledgment. This work was carried out with the partial support of NATO.

Appendix

The plastic cluster model requires a complete **G** matrix and a diagonal **F** matrix in which two M–M stretching force constants are included, one referring to the long H-bridged M–M bonds (f_l) and one to the short nonbridged M–M bonds (f_s). The following equations are easily obtained:

$$\nu_1(A_1) = [(1 + \cos\beta)f_l + f_s + \Delta]^{1/2} \tag{1}$$

$$\nu_2(A_1) = [(1 + \cos\beta)f_l + f_s - \Delta]^{1/2} \tag{2}$$

$$\nu_3(B_1) = [2(1 - \cos\beta)f_l]^{1/2} \tag{3}$$

$$\nu_4(B_2) = [2f_s]^{1/2} \tag{4}$$

$$\nu_5(E) = [2f_l]^{1/2} \tag{5}$$

where $\Delta^2 = [(1 + \cos\beta)f_l + f_s]^2 - 8(\cos\beta)f_lf_s$ and β is the angle between the long M–M bonds.

From eq 1–4, β can be obtained as

$$\cos\beta = (\nu_1^2 + \nu_2^2 - \nu_3^2 - \nu_4^2)/(\nu_1^2 + \nu_2^2 + \nu_3^2 - \nu_4^2)$$

Assuming, reasonably, that $f_l < f_s < 2f_l$ and $\beta = 60 \pm 5°$, we find

$$\nu_1 \sim 2\nu_2 \qquad \nu_4 > \nu_5 > \nu_3$$

The introduction of interaction constants between the stretching of two adjacent M–M bonds gives rise to the following modifications:

(a) f_{ls} (coupling between long and short bonds)

$$\nu_1 = [(1 + \cos\beta)f_l + f_s + 4(2^{1/2})(1 - \cos\beta)^{1/2}f_{ls} + \Delta']^{1/2}$$

$$\nu_2 = [(1 + \cos\beta)f_l + f_s + 4(2^{1/2})(1 - \cos\beta)^{1/2}f_{ls} - \Delta']^{1/2}$$

where $\Delta' = [(1 + \cos\beta)f_l + f_s]^2 - 8\ (\cos\beta)(f_lf_s - 8f_{ls}^2)]^{1/2}$.

(b) f_{ll} (coupling between two long bonds)

$$\nu_1 = [(1 + \cos\beta)(f_l + 2f_{ll}) + f_s + \Delta'']^{1/2}$$

$$\nu_2 = [(1 + \cos\beta)(f_l + 2f_{ll}) + f_s - \Delta'']^{1/2}$$

$$\nu_3 = [2(1 - \cos\beta)(f_l - 2f_{ll})]^{1/2}$$

where $\Delta'' = [(1 + \cos\beta)(f_l + 2f_{ll}) - 8(\cos\beta)f_s(f_l + 2f_{ll})]^{1/2}$.

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[12] Arif, M.; Kettle, S. F. A. *J. Organomet. Chem.* **1983**, *249*, 175.

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Notes

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Formation of a Nickel Carbonyl Cation Containing a Cyclophosphenium Ligand by Hydride Abstraction

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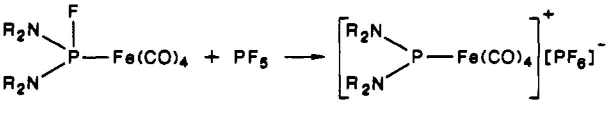
Following the discovery of the first cyclophosphenium cation by Fleming[1] and co-workers, the first metal carbonyl containing a phosphenium cation as a ligand was obtained in this laboratory[2] by direct reaction of the cyclic phosphenium cation with $Fe(CO)_5$ or $Fe_2(CO)_9$. A more effective route to these metal complex cations was found[2] to be halide extraction using a strong Lewis acid as a halide ion acceptor. A typical reaction involving fluoride ion removal is given by



(1)

Muetterties and co-workers[3] were able to extract an OR⁻ group

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[1] Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534.

[2] Montemayor, R. G.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231.

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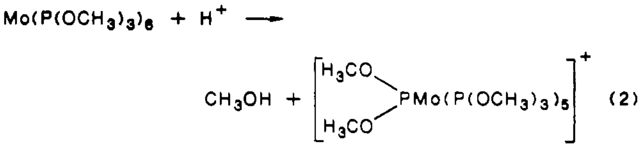
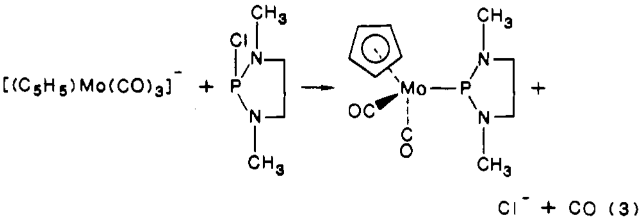
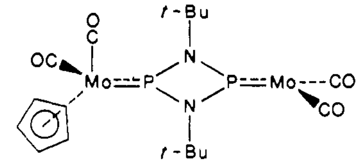
from a $P(OR)_3$ by use of a strong Brønsted acid to generate a phosphenium cation. Their process can be represented by



Paine[4] and co-workers used interaction of a metal carbonyl anion with a diaminochlorophosphine to generate a neutral species containing a formalistic phosphenium cation:

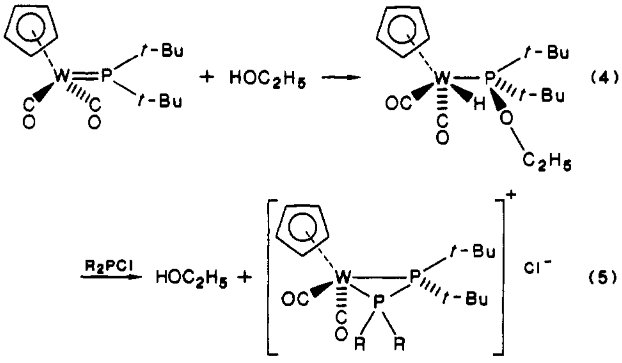


This process can also be considered as originating from halide ion extraction. As noted by Cowley and Kemp[5] in an excellent review on the chemistry of phosphenium ions, Paine and his students[6] have also extended this approach to the synthesis of bimetallic derivatives such as **1**.



1

A somewhat different approach to cation synthesis that ultimately involves halide removal was reported recently by Malisch[7] and his co-workers, who used the metal–phosphorus double bond in the compound $[Cp(CO)_2W{=}PR_2]$ as a starting point. The process as defined by Malisch can be described by



In a sense, this process also involves halide removal from a chlorophosphine, but the process is quite different from the processes described in the original synthesis. The current paper reports synthesis of a new nickel tricarbonyl cyclophosphenium cationic complex by the heretofore unreported process of hydride abstraction. A complex hydride anion is formed.

Table I. Phosphorus-31 NMR Data for Metal Carbonyl Cations and Related Species

compd	δ	J_{PH}, Hz	J_{PF}, Hz
$H_3CNCH_2CH_2N(CH_3)PF$	138	...	1047
$(CO)_4Fe(P(F)N(CH_3)CH_2CH_2NCH_3)$	185	...	1162
$[(CO)_4Fe(PN(CH_3)CH_2CH_2NCH_3)]^+$	300	...	...
$(CO)_3Ni(P(F)N(CH_3)CH_2CH_2NCH_3)$	161	...	−1100
$H_3CNCH_2CH_2N(CH_3)PH$	97	150	...
$(CO)_3Ni(P(H)N(CH_3)CH_2CH_2NCH_3)$	118	280	...
$[(CO)_3Ni(PN(CH_3)CH_2CH_2NCH_3)]^+$	274 ± 2^a 276 ± 1^b		

[a] Anion was $[HB(sec\text{-}Bu)_3]$; THF was solvent. [b] Anion was $[PF_6]^-$; CH_2Cl_2 was solvent.

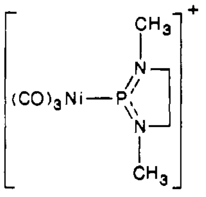
Results and Discussion

Synthesis and Identification of $[(CO)_3Ni(PN(CH_3)CH_2CH_2NCH_3)]^+[HBR_3]^-$. In a recent paper[8] reduction with L-Selectride (Aldrich) of the cyclic complex $H_3CNCH_2CH_2N(CH_3)P(F)Ni(CO)_3$ to give $H_3CNCH_2CH_2N(CH_3)P(H)Ni(CO)_3$ was described. The equation for the process is

$$(CO)_3Ni[P(F)N(CH_3)CH_2CH_2NCH_3] + LiHBR_3 \xrightarrow{THF} R_3B + LiF(s) + (CO)_3Ni[P(H)N(CH_3)CH_2CH_2NCH_3] \quad (6)$$

$$R = sec\text{-butyl}$$

When the reaction mixture resulting from the above process was allowed to sit at −19 °C for 12 days, the color changed from yellow to red-brown and the ^{31}P NMR spectrum indicated the formation of a new phosphorus-containing species. The NMR ^{31}P chemical shift value was consistent with the formation of the new cation **2**. The ^{31}P chemical shift was downfield at 274 ppm from 85% H_3PO_4, used as an external standard. This value is 155 ppm downfield from that of starting compound, $(CO)_3Ni(H)PN(CH_3)CH_2CH_2NCH_3$. As the data in Table I show, a ^{31}P chemical shift of 274 ppm is diagnostic for cationic phosphorus formation. NMR data showed no remaining (cyclodiamino*fluoro*phosphine)tricarbonylnickel. Further ^{19}F spectra gave no evidence for fluoro compounds in solution.



2

The hydride ion transfer is an equilibrium process involving the tri-*sec*-butylboron(III) present in the solution. (The borane is present as a result of the original use of L-Selectride, which was employed as a reducing agent in the reduction of the fluorophosphine.) The equation for the hydride transfer equilibrium process is

$$(CO)_3Ni(P(H)N(CH_3)CH_2CH_2NCH_3) + BR_3 \overset{THF}{\rightleftharpoons} [(CO)_3Ni(PN(CH_3)CH_2CH_2NCH_3)]^+[HBR_3]^- \quad (7)$$

When the system represented by the above equation is cooled to −80 °C, ^{31}P NMR spectra show that the relative concentration of the P–H product increases (ratio A/B = 2.4/1.0). When the temperature is raised to −23 °C, the P–H and P^+ species are present in approximately equal concentrations (ratio A/B =

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1.0/1.0). These facts will be considered later.

If the relative concentrations of free BR_3 and HBR_3^- could be obtained directly from ^{11}B NMR data, it would be possible to obtain a value for the equilibrium constants at −80 and −23 °C and from these constants a ΔH value for the process of cation formation. Unfortunately the ^{11}B NMR data completed up to the present time have not been particularly helpful in establishing BR_3/HBR_3^- concentration ratios. The ^{11}B NMR showed that because an excess of L-Selectride had been used in the original reduction, the major boron containing species in solution at −23 °C was represented by a peak for L-Selectride ($LiHBR_3$) at −7.3 ppm vs. $F_3D\cdot OEt_2$. Free BR_3 in solution at −23 °C was seen as a small, broad peak near 84 ppm. At −80 °C no peak for free R_3B could be detected.

Synthesis of $[(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+[PF_6]^-$ by Halide Extraction. To verify the identity of the cationic nickel complex, it was prepared by a more conventional halide abstraction process by adding equimolar amounts of the fluoride reagents in CH_2Cl_2 rather than in THF.

$$(CO)_3Ni\overline{P(F)N(CH_3)CH_2CH_2N}(CH_3) + PF_5 \xrightarrow[-40\text{ to }+25\text{ °C}]{CH_2Cl_2} [(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+ + [PF_6]^- \quad (8)$$

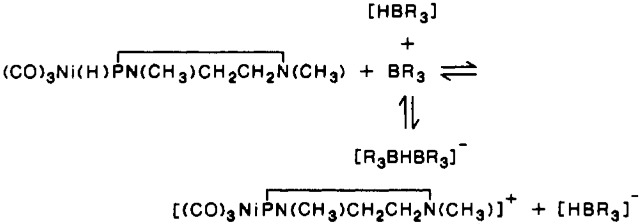
The solution changed from colorless to yellow. The ^{31}P NMR spectrum of the product solution resulting from fluoride extraction showed a chemical shift value of 276 ppm for the complex phosphorus cation. The difference of 2 ppm (274 vs. 276 ppm) in the ^{31}P NMR chemical shift value would be expected when the solvent is changed and possible hydride exchange equilibrium are considered in the THF solution. The data leave little doubt about the validity of the original hydride-transfer process for the formation of the tricarbonyl(phosphenium)nickel cation.

Reaction of $(CO)_3Ni(H_3C\overline{NCH_2CH_2N(CH_3)P}H)$ and $(C_6H_5)_3C^+PF_6^-$. Another Attempt at Hydride Extraction. The "trityl" cation, $[(C_6H_5)_3C]^+$, is widely used as a hydride-extracting reagent in a number of organic systems. It was thus of interest to see if the trityl cation could remove a hydride ion from $(CO)_3Ni(H_3C\overline{NCH_2CH_2N(CH_3)P}H)$ to give the complex cation. When reagents were mixed at −80 °C, all dissolved in CH_2Cl_2 and the color of the system changed from yellow to very dark red, but the ^{31}P NMR gave no evidence for the expected $[-P^+-][PF_6]^-$ compound. Decomposition products plus the signal for $(CO)_3Ni(H_3CNCH_2CH_2N(CH_3)PF)$ were seen as the system was warmed from −80 °C. The system went very dark brown. In our hands, up to the present time, the use of the trityl cation as a hydride acceptor did not give a satisfactory route to the desired nickel cation complex, but further work seems justified.

Comparisons of the Cation System in the Presence of the PF_6^- and HBR_3^- Anions. While the ^{31}P NMR spectrum indicates clearly that cation **2**, $[(CO)_3N\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+$, is present in solutions containing both the HBR_3^- and the PF_6^- anions, a number of significant differences exist that deserve comment. One of the most obvious contrasts is the color of the cation in the presence of different anions. When cation **2** was made by fluoride extraction, the solution color was a clear yellow; when it was made by hydride extraction, the solution color was red-brown, suggesting possible perturbation of the color center or the presence of impurities. At the present time we believe color differences are a result of decomposition since such yellow to red-brown color development is seen during the decomposition of the cyclic and acyclic $(R_2N)_2PH$ species and their metal carbonyl adducts.

Color changes can also result from interaction of a borane acid with a phosphine substituted metal carbonyl. Recently Paine, Nöth, and their co-workers[9] reported that purple (Cp)Mo(CO)$_2$[P(Ph){N[Si(CH$_3$)$_3$]$_2$}] will add BH_3 to give green (Cp)Mo(CO)$_2$[P(BH$_3$)(Ph){N[Si(CH$_3$)$_3$]$_2$}], which contains the Mo–H–B–P linkage. Such a reaction is accompanied by large shifts in the ^{31}P resonance (about 266 ppm). Since NMR shifts in this study did not correlate with color changes (^{31}P shift was that expected for the cation), decomposition products remain the preferred explanation for the red-brown color.

The ^{11}B NMR showed that BR_3 was not present at −80 °C and the compound $(CO)_3Ni\overline{P(H)N(CH_3)CH_2CH_2N}(CH_3)$ was the dominant nickel species. The following equilibrium is suggested:



$$\begin{array}{ccc} & [HBR_3]^- & \\ & + & \\ (CO)_3Ni(H)\overline{PN(CH_3)CH_2CH_2N}(CH_3) + & BR_3 & \rightleftharpoons \\ & \upharpoonleft\downharpoonright & \\ & [R_3BHBR_3]^- & \\ \end{array}$$
$$[(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+ + [HBR_3]^-$$

Since the solution contained an excess of HBR_3^- from the original reduction operation, this anion could interact with BR_3 at lower temperature to give the double ion of the type reported by Brown and co-workers.[10] Such an equilibrium would explain the ^{11}B NMR observations and existence of the nonionic B–H species as the preferred compound at low temperature.

Experimental Section

Synthesis of $[(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+[HB(\textit{sec}\text{-}Bu)_3]^-$. The literature synthesis[8] of $(CO)_3Ni(H)PN(CH_3)CH_2CH_2N(CH_3)$ by reduction of the fluorocomplex with L-Selectride (Aldrich) was used. The solution from the above reduction stood for 12 days at −19 °C in an NMR tube. A dark red-brown color developed. The cation was identified by NMR.

Synthesis of $[(CO)_3Ni\overline{PN(CH_3)CH_2CH_2N}(CH_3)]^+[PF_6]^-$. A 9-mm-o.d. NMR tube equipped with a 100-mL gas expansion bulb, a stopcock, and ground-glass joint was the reaction vessel. On top of about a 1.0-mmol sample of $(CO)_3Ni(F)PN(CH_3)CH_2CH_2N(CH_3)$ dissolved in 1 mL of CH_2Cl_2, an equimolar quantity of PF_5 was frozen. The system was monitored by ^{31}P NMR. At −40 °C and up to +25 °C, NMR showed the signal for $[(CO)_3NiPN(CH_3)CH_2CH_2N(CH_3)]^+[PF_6]^-$. Data are given in Table I.

Reaction of $(CO)_3Ni(H)\overline{PN(CH_3)CH_2CH_2N}CH_3$ with Trityl Hexafluorophosphate, $[(C_6H_5)_3C]^+[PF_6]^-$. A 1.4-mmol sample of $(CO)_3Ni(H)PN(CH_3)CH_2CH_2NCH_3$ was dissolved in 1 mL of dry CH_2Cl_2 and then a 1.0-mm sample of $[(C_6H_5)_3C]^+[PF_6]^-$ in 1.0 mL of CH_2Cl_2 was added at −80 °C. The reaction system was warmed to −40 °C where reaction took place. The system did not change appreciably as the temperature was raised to 23 °C.

Acknowledgment. Major support of this work by the National Science Foundation through Grant No. CHE 7920313 is gratefully acknowledged.

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Dinitrogen Pentoxide. New Synthesis and Laser Raman Spectrum

William W. Wilson and Karl O. Christe*

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Dinitrogen pentoxide, the anhydride of nitric acid, was first prepared in 1849 from the reaction of Cl_2 with dry $AgNO_3$ at 60 °C.[1] Subsequent methods involve either the dehydration of

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