Organometallics **1989**, *8*, 2147–2153 2147

Science Foundation and by the PRC National Natural Science Foundation. Additional support was provided by NSF Grant CHE-8818696. We are grateful to Professor Josef Takats and Dr. Gong-Yu Kiel for a gift of $Os(CO)_5$ and to Dr. Paula Bogdan for helpful discussions and suggestions on the synthesis of $Ru(CO)_5$.

Registry No. $Fe(CO)_5$, 13463-40-6; $Ru(CO)_5$, 16406-48-7; $Os(CO)_5$, 16406-49-8; PPh_3, 603-35-0; $(CH_3)_3NO$, 1184-78-7.

Supplementary Material Available: Additional values are given of k_{obsd} for reactions (eq 2) at different concentrations of $(CH_3)_3NO$ and different temperatures (Table S1) (2 pages). Ordering information is given on any current masthead page.

New Approaches to Heteroatomic Chelation of Early and Late Transition Metals. Synthesis and Characterization of Cyclometallaphosphoranimine- and Cyclometallaphosphoraniminatophosphanes (and Arsanes) of Mo(0), W(0), Rh(I), and Ir(I) Derived from Novel Heterodifunctional Phosphorus and Arsenic Ligands

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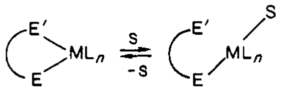
Oxidation of one phosphorus in $Ph_2PCH_2PPh_2$ and in $Ph_2PC_2H_4AsPh_2$ with Me_3SiN_3 gives new heterodifunctional ligands with phosphorus(III) (or arsenic(III)) and nitrogen base centers. Chelate complexes $LL'M(CO)_4$ (M = Mo, W), formed by $Me_3SiN{=}PPh_2CH_2PPh_2$ (**1**, LL'), have been fully characterized by ^{31}P, ^{29}Si, and ^1H NMR and IR spectroscopy. **1** reacts with activated fluoroaromatics (pentafluoropyridine and pentafluorobenzonitrile) eliminating Me_3SiF to give quantitative yields of the compounds $XN{=}PPh_2CH_2PPh_2$ (**5**, X = p-C_6F_4CN; **6**, X = p-C_5F_4N) wherein the N atom of the ligand bears a fluoroaromatic substituent. Exclusive substitution via the para position of the fluoroaromatic ring occurs. $[Rh(CO)_2Cl]_2$ reacts with **1**, **5**, and **6** to form the corresponding monomeric chelate complexes with both P and N coordinated to Rh(I). These complexes (**14**, **7**, **8**) show characteristic $^1J_{PRh}$ values of 160–170 Hz indicating direct Rh–P(III) binding. Smaller coupling with the remote P(V) atom is also observable. The CO is cis to the P(III) center. The N-silylated As/P derivative $Me_3SiN{=}PPh_2CH_2CH_2AsPh_2$ (**9**) also forms the chelated $LL'Rh(CO)Cl$ complex (**10**) which behaves very similarly to the complex derived from **1**. ν_{PN} values for the coordinated iminato phosphorane unit (1120–1125 cm^{-1} in Mo(0) and W(0) complexes **2** and **3** and 1142 cm^{-1} for N-silylated complexes of Rh from **1** and **9** (**14** and **10**)) shift to significantly lower values in the fluorocarbon chelates (**7**, **8**) (1080 cm^{-1}) as the result of the significant reduction in electron density at the nitrogen. $[M(cod)Cl]_2$ (M = Rh, Ir) complexes eliminate Me_3SiCl in reactions with **1** and **9** to form the metallacycles $\overline{N{=}PPh_2(CH)_2)_nEPh_2M}(cod)$ (**4**, M = Ir, E = P, n = 1; **13**, M = Rh, E = P, n = 1; **11**, M = Rh, E = As, n = 2; **12**, M = Ir, E = As, n = 2). These monomeric compounds that contain a metal–nitrogen σ bond and a coordinated P or As atom are characterized by a marked low-field ^{31}P NMR shift of the P(V) center suggesting substantial delocalization in the P=N—M portion of the molecule. The ν_{PN} characteristic value for these complexes (**4**, **13**, **11**, **12**) is approximately 1230 cm^{-1}. These latter compounds provide a new class of nitrogen-bonded metallacycles of the late transition metals.

Introduction

Whereas a large class of homoatomic chelated and bridged transition-metal complexes based on the alkane diphosphanes $R_2P(CR'_2)_nPR_2$ are known,[1-4] extension of these frameworks by introducing an additional heteroatomic donor site (e.g., partial oxidation) to achieve systems of heteroatomic bridged complexes is limited. This is in part due to the difficulties involved in the chemical modifications of the ligands themselves to create heteroatomic reactive sites,[5] sites which will be particularly suitable for binding the metals of interest. Heterodifunctional ligands also provide contrasting binding properties for metals, and thus effective catalysts may be generated from complexes of bifunctional chelate ligands in which one substituent is more loosely bound than the other so that an equilibrium providing access to a reactive intermediate can be established.



(1)

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(3) McAuliffe, C. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987, Vol. 2, Chapter 14.

(4) For a review on the use of dppm as bridging ligands for bimetallic compounds, see: Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *112*, 99.

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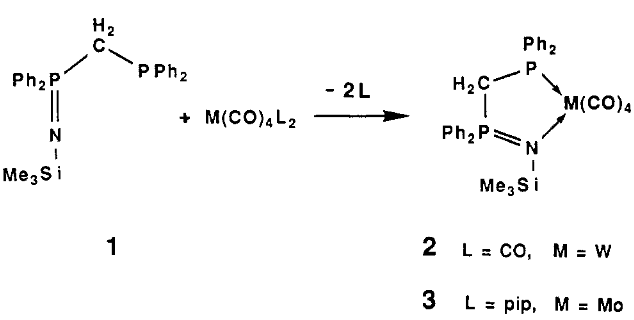
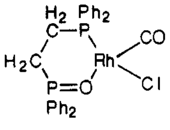
Scheme I



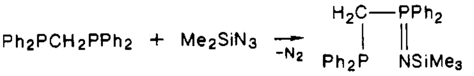
Such a sequence has been demonstrated[6] in the catalytic carbonylation of methanol mediated by the heterodifunctional diphosphane monoxide complex A of Rh(I).



A

The unique reactivities of transition metals with heteroatomic chelates has sparked recent interest in the synthesis of different types of heterodifunctional ligands.[7] A literature survey shows that directed synthetic strategies, which can be applied to the synthesis of a set of ligands in which structure and substituents are varied to "tune" the reactivity of one of the interacting heteroatoms, have not been established. A unified approach to synthesis of heterodifunctional ligands would present considerable opportunities for the design and construction of chemo- and stereoselective ligands, which in turn would provide access to a variety of metal complexes with useful catalytic properties.

We have developed[8] an approach to the synthesis of heterodifunctional ligands via the well-known Staudinger reaction.[9] Partial oxidation of the alkane-bridged diphosphanes (eq 2) with Me$_3$SiN$_3$ also introduces a reactive trimethylsilyl functionality on the nitrogen which provides additional reactivity. This approach is general and may be applied to diphosphanes of any alkane chain length.[10] Phosphoraniminato ligands, R$_3$PN$^-$ (isoelectronic with R$_3$PO), have been extensively used to stabilize both transition[11-15] and actinide[16] metal compounds. The presence of both the phosphoraniminato and the phosphane functionalities in 1 presents the possibility of their cooperative interaction with the transition metals. Herein, we report a general synthetic approach to the new class of heterodifunctional phosphane and arsane ligands and demonstrate their reactivity toward the early and late transition metals. The latter has led to new classes of metallacyclic compounds: cyclometallaphosphoraniminatophosphanes (or arsanes). We have presented a preliminary report of examples of the former type.[17]



$$\mathrm{Ph_2PCH_2PPh_2} + \mathrm{Me_2SiN_3} \xrightarrow[-\mathrm{N_2}]{} \begin{array}{ccc} \mathrm{H_2C} & \text{—} & \mathrm{PPh_2} \\ | & & \| \\ \mathrm{Ph_2P} & & \mathrm{NSiMe_3} \end{array} \qquad (2)$$

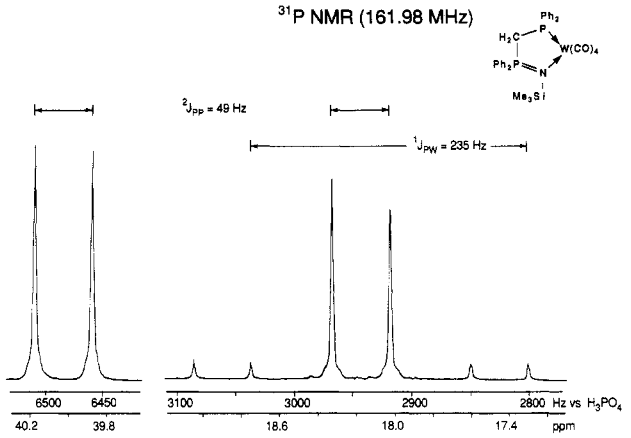


Figure 1. Proton-decoupled Fourier transform ^{31}P NMR spectrum of Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$W(CO)$_4$ (2).

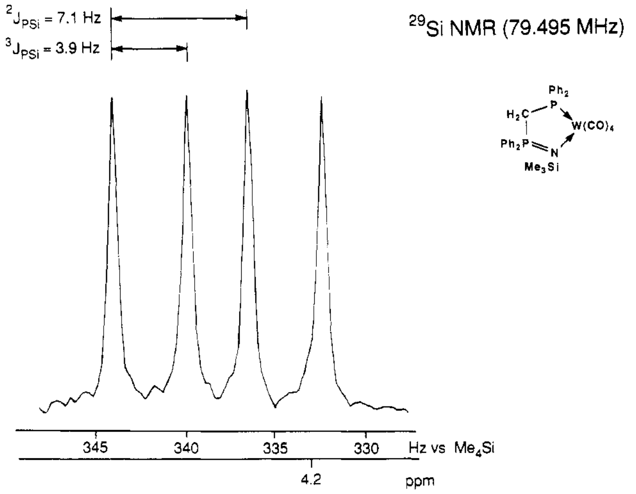


Figure 2. ^{29}Si (INEPT) spectrum of Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$W(CO)$_4$ (2).

Results and Discussion

Cyclometallaphosphoraniminephosphanes of Some Early Transition Metals. Tungsten and molybdenum carbonyls reacted cleanly with 1 to give the new cyclo-

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[12] (a) Roesky, H. W.; Seseke, U.; Noltemeyer, M.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1109. (b) Roesky, H. W.; Katti, K. V.; Scholtz, U.; Herbst, R.; Egert, E.; Sheldrick, G. M. *Z. Naturforsch., B* **1986**, *41B*, 1509.

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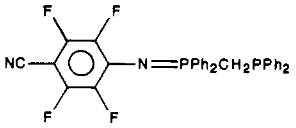
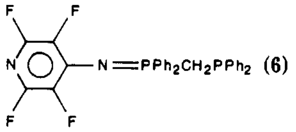
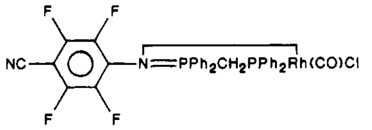
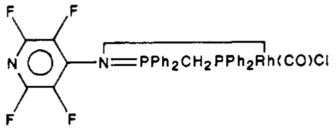
Table I. Phosphorus-31 NMR[a] and Infrared[b] Spectroscopic Data for Phosphoraniminephosphanes (or Arsane) and Their Metal Complexes and Iminato Compounds

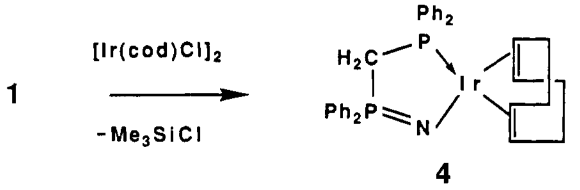
compound	$\sigma_{P^{III}}$	σ_{P^V}	$^2J_{PP}$, J_{P-M}, Hz	$\nu_{P=N}$, cm^{-1}
$Me_3SiN{=}PPh_2CH_2PPh_2$ (1)	−28.20	−1.38	57.74	1310
 (5)[c]	−30.12	13.04	53.60	1225
 (6)	−29.93	13.20	52.96	1225
$Me_3SiN{=}PPh_2(CH_2)_2AsPh_2$ (9)	...	1.83	...	1310
$Me_3SiNPPh_2CH_2PPh_2W(CO)_4$ (2)[d]	18.17	40.02	48.85; $^1J_{P-W}$ = 235	1120
$Me_3SiNPPh_2CH_2PPh_2Mo(CO)_4$ (3)[e]	27.22	33.29	50.80	1125
$NPPh_2CH_2PPh_2Ir(cod)$ (4)	20.13	61.23	34.98	1230
$NPPh_2CH_2PPh_2Rh(cod)$ (13)	32.97	52.17	44.10; $^1J_{P-Rh}$ = 158.6, $^2J_{P-Rh}$ = 7.5	1235
$Me_3SiNPPh_2CH_2PPh_2Rh(CO)Cl$ (14)	37.64	24.36	31.10; $^1J_{P-Rh}$ = 168.6, $^2J_{P-Rh}$ = 4.0	1142
 (7)[f,g]	39.75	43.69	30.77; $^1J_{P-Rh}$ = 165.2	1080
 (8)[g,h]	38.85	42.17	31.25; $^1J_{P-Rh}$ = 167.0	1080
$Me_3SiNPPh_2(CH_2)_2AsPh_2Rh(CO)Cl$ (10)[i]	...	26.57	...; $^2J_{P-Rh}$ = 8.70	1140
$NPPh_2(CH_2)_2AsPh_2Rh(cod)$ (11)	...	55.45	...; $^2J_{P-Rh}$ = 9.20	1230
$NPPh_2(CH_2)_2AsPh_2Ir(cod)$ (12)	...	60.45		1235

[a] All spectra in $CDCl_3$; ppm vs 85% H_3PO_4. [b] All spectra in $CHCl_3$; cast. [c] $^4J_{P^VF}$ = 5.70 Hz; $^6J_{P^VF}$ = 1.50 Hz; $^6J_{P^{III}F}$ = 2.05 Hz. [d] ν_{CO} = 2007 (s), 1920 (vs), 1884 (vs), 1866 (vs) cm^{-1}. [e] ν_{CO} = 2012 (s), 1916 (vs), 1885 (vs), 1860 (vs) cm^{-1}. [f] ν_{CO} = 1972 cm^{-1}. [g] The proximity of $^4J(^{31}P-^{19}F)$ and $^2J(^{31}P-^{103}Rh)$ precluded the measurement of these parameters. [h] ν_{CO} = 1970 cm^{-1}. [i] ν_{CO} = 1976 cm^{-1}.

metallaphosphoraniminephosphanes 2 and 3 in good yields (Scheme I). Although in general the presence of easily replaceable functionalities (such as nitriles or amines) is required for the facile elimination of more than one CO group from $W(CO)_6$, our new ligands do not require such enhancement. Our ligands provide bifunctionality from a "soft" phosphorus(III) center (which has a predisposition for combination with soft metals) and a "hard" nitrogen center (which is predisposed to combination with early transition metals) so that the complex formation process is favored in a variety of situations. These different binding propensities are probably also responsible for the high kinetic and thermal stabilities of the new metallacycles 2 and 3 which represent the first examples of a potentially large class of cyclometallaphosphoraniminephosphanes of early transition metals. Compounds 2 and 3 are air-stable, crystalline solids, readily soluble in common organic solvents, and are monomeric in solution.

Phosphorus-31 NMR data are given in Table I. The spectrum of the ligand 1 consisted of two sharp doublets centered at −28.20 and −1.38 ppm which are readily attributable to phosphane and phosphoranimine groups, respectively. Two doublets centered at 18.17 and 40.02 ppm (the latter signal showing a large $^1J(^{31}P-^{183}W)$ of 235 Hz) were the characteristic features in the ^{31}P NMR spectrum of the metallacycle 2 (Figure 1). The large shielding of the phosphane unit compared to the phosphoranimine center in 2 is probably a consequence of the interplay of two effects: (a) the delocalization of electronic charge along the $Ph_2P{=}N{-}W^0$ framework and (b) the net transfer of the electron density from the W(0) to the phosphane unit. The $^{31}P\{^1H\}$ NMR spectroscopic behavior of the Mo(0) metallacyclic compound 3 was similar to that of 2 (Table I). The ^{29}Si (INEPT) NMR spectroscopy of 2 (Figure 2) and 3 clearly showed the coupling of silicon to both the phosphane and phosphoranimine phosphorus nuclei across two and three bonds, respectively ($^2J(^{29}Si-^{31}P)$ = 7.09 and $^3J(^{29}Si-^{31}P)$ = 3.90 Hz in 2). The operation of an efficient through-bond $Me_3Si-N-M-PPh_2$ (M = W in 2, M = Mo in 3) electronic interaction suggestive of significant electron delocalization within these five-membered rings is evident from these observations. The disposition of the carbonyl groups in the octahedral complexes 2 and 3 is cis as confirmed by IR spectroscopy (Table I).

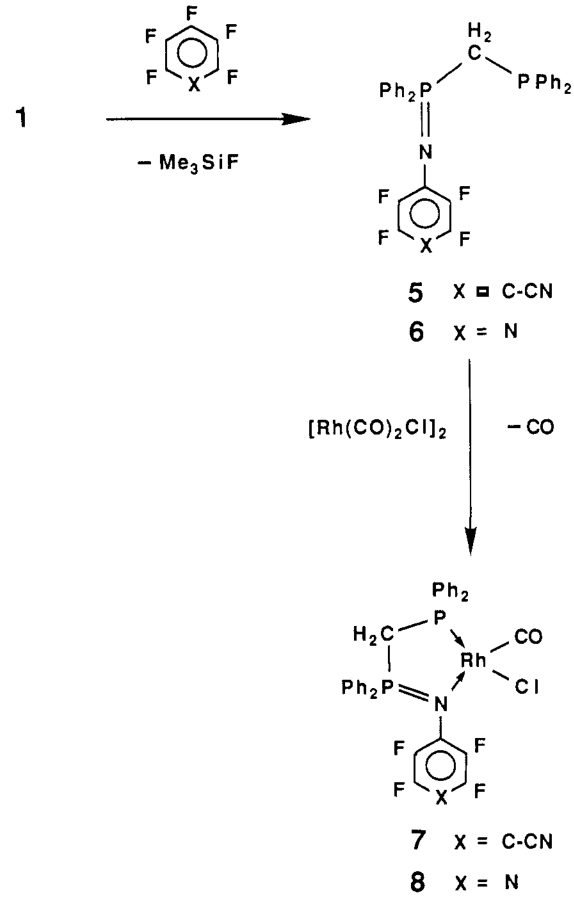
Scheme II



4

Cyclometallaphosphoranimine- and Cyclometallaphosphoraniminatophosphanes of Late Transition Metals. The presence of a reactive Si–N bond in 1 presents the possibility of σ-bond formation with metals via elimination of trimethylsilyl halide. This aspect has

Scheme III

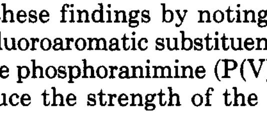


been demonstrated in the reaction of 1 with $[Ir(cod)Cl]_2$ (Scheme II) wherein facile elimination of Me_3SiCl occurred at 25 °C to give the metallacycle 4 containing an Ir–N σ bond in good yields. A closely related metallacyclic compound containing a Rh–N σ bond which was obtained from the reaction of $[Rh(cod)Cl]_2$ with 1 has been characterized previously.[17] The monomeric compound 4 is an air-stable, crystalline solid.

The $^{31}P\{^1H\}$ NMR spectrum of 4 showed two sharp doublets centered at 20.13 and 61.23 ppm, respectively (Table I). Following the ^{31}P NMR assignments of $\overline{NPPh_2CH_2PPh_2Rh}(cod)$[17] the high-field signal was assigned to the phosphane and the low-field signal to the phosphoraniminato functions. Although the spectroscopic data of 2, 3, and 4 (Table I) cannot be directly compared due to the presence of M–N σ bonding in the latter compound, a common feature underlying the spectroscopic trends of these compounds is the shielding of the phosphorus(III) functionality compared to the phosphoraniminato unit. Delocalization of charge on the $Ph_2P{=}N{-}M$ unit, particularly when a metal–nitrogen σ bond exists as in 4, may be envisaged.

Scheme III illustrates reactions that convert 1 to new heterodifunctional ligands in which the donor ability of the nitrogen is modified by introduction of a fluoroaromatic substituent on N. The new fluoroaromatic phosphoranimine phosphanes 5 and 6 were obtained in almost quantitative yields as air-stable, crystalline solids. A significant deshielding of the phosphoranimine phosphorus (Table I, Figure 3) in 5 and 6 compared to 1 arises from the electronic effects exerted by the electronically demanding fluoroaromatic substituents.

Reactions of 5 and 6 with $[Rh(CO)_2Cl]_2$ in dichloromethane at 25 °C (Scheme III) gave the new metallacycles 7 and 8, respectively. The $^{31}P\{^1H\}$ NMR spectrum of 7 (Table I, Figure 4) also showed remarkable differences in the chemical shifts of the P(III) and P(V) phosphorus units compared to those of the parent ligand 5. The large difference of 43 ppm between the chemical shifts of the P^{III} and P^{V} centers in 5 was reduced to only 3.9 ppm in 7 (Table I, Figure 4). Similar behavior was demonstrated by 8 (Table I). Such small differences in NMR chemical shifts between centers with such a large formal valence state difference (P^{III} vs P^{V}) appears to be unprecedented. We rationalize these findings by noting that the highly electronegative fluoroaromatic substituent would decrease the basicity of the phosphoranimine (P(V)) nitrogen which in turn will reduce the strength of the coordination interaction of this nitrogen with the Rh(I) center. However, the electron density from the electron-rich Rh(I) center can easily drift via the imine nitrogen onto the fluoroaromatic substituent. This electronic effect possibly leads to reduced back-bonding of Rh(I) with the P(III) phosphane center, and this is manifested by the unusual proximity of the shifts for the two kinds of phosphorus in 7 and 8. A similar electronic interaction between the phosphoranimine phosphorus and the fluoroaromatic substituent through an extended conjugated path such as



may account for the slight deshielding of the phosphoranimine phosphorus (two bonds away from Rh(I)) compared to the directly bound Rh(I)–P(III) center in 7 and 8. These dramatic electronic changes induced by fluoroaromatic substituents illustrate the chemical flexibility offered by the ligands of the type 1.

Further characterization of 7 and 8 was provided by ^{13}C NMR spectroscopy, which showed $^2J(^{13}C-^{31}P)$ values of 18.55 and 19.20 Hz, respectively, indicative of a cis relationship between the CO and the phosphane substituents

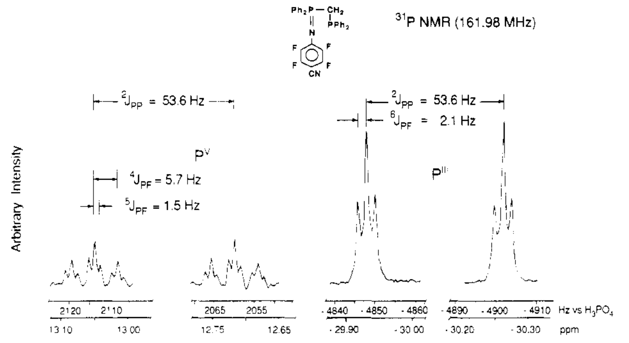


Figure 3. Proton-decoupled Fourier transform ^{31}P NMR spectrum of 5.

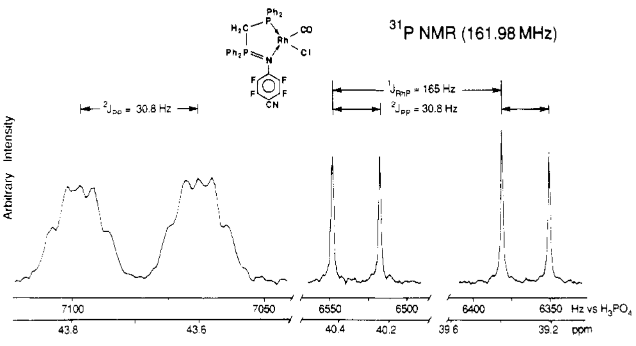
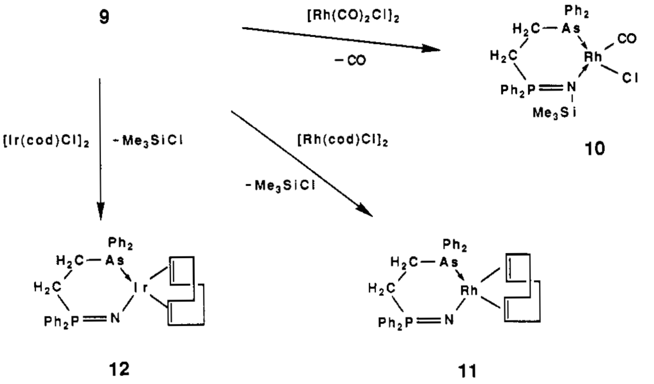


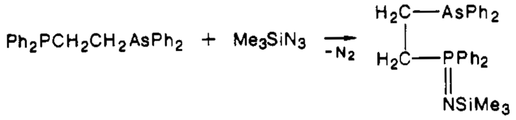
Figure 4. Proton-decoupled FT ^{31}P NMR spectrum of 7.

Scheme IV



in these two metallacycles. In addition, ν_{CO} values of 1972 and 1970 cm^{-1} for **7** and **8**, respectively, are consistent with the proposed cis structures for these compounds.

The closely related arsenic ligand $Me_3SiN{=}PPh_2(CH_2)_2AsPh_2$ (**9**) reacts similarly with Rh(I) and Ir(I) complexes. The new heterodifunctional silylated ligand **9** was obtained from a Staudinger[9] reaction (eq 3) with

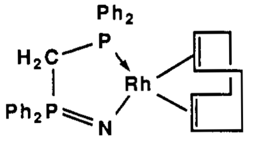


$$Ph_2PCH_2CH_2AsPh_2 + Me_3SiN_3 \xrightarrow[-N_2]{} \begin{array}{l} H_2C{-}AsPh_2 \\ \; | \\ H_2C{-}PPh_2 \\ \qquad \| \\ \qquad NSiMe_3 \end{array} \quad (3)$$

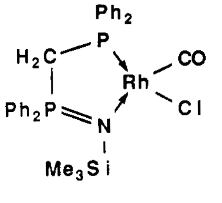
9

ARPHOS. The oxidation of ARPHOS was selective at phosphorus even when the reaction was carried out in the presence of excess amounts of Me_3SiN_3. The preparation of a new class of six-membered metallacycles (the cyclometallaphosphoranimine- and cyclometallaphosphoraniminatoarsanes) obtained from the new ligand **9** and Rh(I) and Ir(I) complexes is outlined in Scheme IV. The resultant metallacycles **10**, **11**, and **12** are airstable, crystalline solids and are monomeric in solution.

The $^{31}P\{^1H\}$ NMR spectra of **10** and **11** consisted of sharp doublets (due to $^2J(^{31}P{-}Rh)$ coupling across two bonds) centered at 26.57 and 55.45 ppm, respectively (Table I). We attribute the marked deshielding of the phosphoraniminato phosphorus in **11** and **12** (σ_{P^V} = 55.45 and 60.45 ppm, respectively) compared to that in **10** (σ_{P^V} = 26.57 ppm) to the presence of M–N σ bonds in the former. Similar chemical shift relations were noted in the Rh(I) metallacycles **13** and **14**, which respectively contain a M–N σ and a nitrogen coordinate donor bond.[17]



13

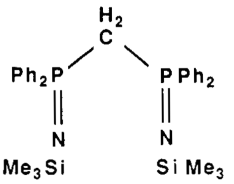


14

The reactivity of the $[M(cod)Cl]_2$ (M = Rh, Ir) derivatives with **9** follows the same pattern demonstrated by derivatives of **1** to give, in all cases, metallacycles with M–N σ bonds. The difference in reactivity between the cod and carbonyl complexes (Scheme IV) with **9** is significant, and we rationalize this difference by presuming that Rh(I) or Ir(I) complexes react with **9** (or **1**) to first form a monomeric complex via monodentate coordination of the ligand through the arsane (or phosphane) end. Displacement of the relatively labile CO by the nitrogen base yields a stable 16-electron complex which then cannot eliminate Me_3SiCl to form an imide unless another ligand can be provided to stabilize the formally 14-electron imide product which would arise from this elimination. In contrast cod might not be as easily displaced completely so in this case a sequence can be visualized in which the nitrogen donor site coordinates to the Rh(I) or Ir(I) center forcing the cod substituent to act as a 2-electron donor. This intermediate may eliminate Me_3SiCl to form the imide **11** (or **12**) which is immediately stabilized as a 16-electron species by reestablishment of the cod as a 4-electron donor. The metallacycles **4** and **11**–**13** thus formed represent the first examples of compounds containing σ bonds between the iminato nitrogen and the late transition metals. Dehnicke et al. have demonstrated that the phosphoranimine ligands of the type **15**, in general, coordinate as 1-, 2-, or 4-electron donors with the late transition metals,[13,14] and Roesky et al. have shown that both of the phosphoranimine derivatives **15** and **16** are

$Ph_3P{=}NSiMe_3$

15



16

excellent synthons for formation of metal–nitrogen σ bonds with early transition metals.[11,12] Likewise Dilworth et al.[15] have prepared Ti(IV) derivatives with Ti–N σ bonds from **15** and its methyldiphenyl analogue. We have also found that the silylated phosphoranimine derivatives **15** and **16** alone do not lead to the formation of M–N σ bonds in their reactions with the complexes $[Ir(cod)Cl]_2$ or $[Rh(cod)Cl]_2$ involving "late" transition metals. We surmise that the formation of M–N σ bonds with "late" transition metals as in **4**, **11**, **12**, and **13** is probably due to the assistance of cooperative interactions of the phosphane, Ph_2P (or arsane, Ph_2As), and the phosphoraniminato, $Ph_2P{=}N{-}$, functionalities in **1** and **9**.

The existence of the postulated coordination interaction between arsenic and the Rh(I) or Ir(I) center in **10**, **11**, or **12** is by no means evident because of the lack of appropriate magnetically active nuclei. However, the higher nucleophilicity of a Ph_2As unit (which exists in **9**) compared to the Ph_2P group (which exists in **1**, **5**, and **6**) should favor stronger metal–arsenic interactions in these compounds. This is already evident from the high kinetic and thermal stabilities exhibited by these six-membered metallacycles **10**–**12**. Furthermore, the ^1H, ^{13}C, and ^{29}Si NMR spectroscopic data of **10**, **11**, and **12** are consistent with the structures proposed.

Infrared Spectroscopic Trends. Infrared spectroscopic data for $\nu_{P{=}N}$ are given in Table I. Generally, the strongest band between 1350 and 1050 cm^{-1} is due to $\nu_{P{=}N}$ in compounds containing this feature. Electronegative substituents on the phosphoranimine nitrogen decrease the P=N bond strength with a concomitant decrease in the stretching frequency. This effect may be seen by comparing $\nu_{P{=}N}$ through the series **1** to **2** or **3** (Table I). The substantial decrease in the $\nu_{P{=}N}$ on metalation of the phosphoranimine nitrogen is herein attributed to a weakening of the P=N bond; this decrease ranges from 170 to 180 cm^{-1} in complexes that contain metal–nitrogen coordinate bonds (i.e., in **2**, **3**, **7**, **8**, **10**, **14**). A decrease of 70–80 cm^{-1} is observed in metallacycles that contain metal–nitrogen σ bonds (i.e., in **4**, **11**–**13**). Similar trends in the IR spectroscopic data have been observed in a number of related cyclic and acyclic phosphoranimine– and phosphoraniminato–transition-metal complexes.[11-15,18,19]

Summary and Conclusions

The readily accessible diphosphane dppm and related materials can be easily converted to a series of novel heterodifunctional ligands, phosphoranimine- and phosphoraniminatophosphanes or phosphoranimine- and phosphoranimatoarsanes, which possess an extensive chemistry clearly showing their heterodifunctionality. Chelate complexes and iminato ligation to form M–N σ bonds are readily formed according to the chemistry presented by the metal. In addition a series of unique reactions (Scheme III) allows judicious modification of the basicity at nitrogen. This kind of chemical flexibility, which has not previously been demonstrated, should allow the design of transition-metal–heteroatomic chelate compounds with optimized metal–nitrogen or metal–phosphine interactions for use in homogeneous catalysis.

Experimental Section

All experimental manipulations were performed under an atmosphere of dry argon. Solvents were dried and distilled prior to use. dppm, ARPHOS, and Me_3SiN_3 were commercial materials obtained from Aldrich. Compound 1 was prepared as previously described.[8]

^1H, ^{19}F, ^{31}P, and ^{29}Si NMR spectra were obtained on a Bruker WH 400 instrument (operating at 400.13, 376.40, 161.97, and 79.50 MHz, respectively) using $SiMe_4$, $CFCl_3$, 85% H_3PO_4, and $SiMe_4$, respectively, as the external standards. An INEPT sequence was employed to enhance signals in the ^{29}Si NMR spectra.[20] In all the spectroscopic studies $CDCl_3$ was used as both the solvent and the internal lock. Positive shifts lie downfield of the standard in all cases. Solution molecular weight measurements were performed in dibromomethane solution with a Mechrolab 301A vapor phase osmometer.

Synthesis of $Me_3Si\overline{N{=}PPh_2CH_2PPh_2W}(CO)_4$ (2). A solution of **1** (3.557 g, 7.54 mmol) in dry toluene (50 mL) was added dropwise (15 min) to a suspension of $W(CO)_6$ (2.657 g, 7.54 mmol) in the same solvent (50 mL). The reaction mixture was heated under reflux, and the evolution of CO was indicated by a gas bubbler. The progress of the reaction was monitored by IR spectroscopy. The reaction was complete in about 20 h. The intense yellow solution that formed was allowed to cool to room temperature, and the solvent was removed in vacuo to leave analytically pure **2** (yield, after washing the product with hexane (5 mL), 5.03 g, 87%; yellow microcrystals; mp 165 °C dec). Anal. Calcd for $C_{32}H_{31}NO_4P_2SiW$: C, 50.00; H, 4.04; N, 1.82. Found: C, 49.97; H, 4.02; N, 1.81. ^1H NMR ($CDCl_3$): phenyl rings δ 7.27, 7.55, 7.92 (m, 20 H); PCH_2P methylene δ 3.82 (dd, 2 H, $^2J_{HP}$ = 11.15, 7.25 Hz). ^{29}Si NMR (INEPT; $CDCl_3$) δ 4.26 (dd, 1 Si, $^2J_{P^{V}Si}$ = 7.09, $^3J_{P^{III}Si}$ = 3.90 Hz).

Synthesis of $Me_3Si\overline{N{=}PPh_2CH_2PPh_2Mo}(CO)_4$ (3). A solution of **1** (0.621 g, 1.31 mmol) in dry dichloromethane (50 mL) was added dropwise (30 min) to a solution of $Mo(CO)_4(pip)_2$ (pip = piperidine) (0.498 g, 1.31 mmol) in the same solvent at 25 °C. The reaction mixture was stirred under reflux for 1 h before the solvent was removed in vacuo to leave **3** (which was recrystallized from CH_2Cl_2–hexane) (yield 0.79 g, 89%; pale yellow cubic crystals; mp 178 °C dec). Anal. Calcd for $C_{32}H_{31}NO_4P_2MoSi$: C, 56.55; H, 4.56; N, 2.06. Found: C, 56.49; H, 4.47; N, 2.06. ^1H NMR ($CDCl_3$): phenyl rings δ 7.26, 7.54, 7.91 (m, 20 H); PCH_2P methylene δ 3.81 (dd, 2 H, $^2J_{HP}$ = 11.05, 7.10 Hz). ^{29}Si NMR (INEPT; $CDCl_3$) δ 2.26 (dd, 1 Si, $^2{}_{JP}{}^{V}{}_{Si}$ = 6.93, $^3J_{P^{III}Si}$ = 3.14 Hz).

Synthesis of $\overline{N{=}PPh_2CH_2PPh_2Ir}(cod)$ (4). A solution of **1** (0.186 g, 0.39 mmol) in dichloromethane (25 mL) was added dropwise (15 min) to a stirred dichloromethane (25 mL) solution of $[Ir(cod)Cl]_2$ (0.132 g, 0.197 mmol) at 25 °C. An instantaneous color change from pale orange to red occurred on mixing. The mixture was stirred at room temperature for 6 h before the solvent was removed in vacuo to yield an analytically pure dichloromethane solvate of **4** (yield, after washing the product with hexane (5 mL), 0.28 g, 91%; red microcrystalline; mp 190 °C dec). Anal. Calcd for $C_{34}H_{36}Cl_2NP_2Ir$: C, 52.10; H, 4.59; N, 1.78; Cl, 9.05. Found: C, 52.17; H, 4.57; N, 1.76; Cl, 9.10. ^1H NMR ($CDCl_3$): phenyl rings δ 7.29, 7.50, 7.80 (m, 20 H); PCH_2P methylene δ 3.72 (dd, 2 H, $^2J_{HP}$ = 9.90, 7.51 Hz); cod olefinic δ 5.25 (br, 2 H), 5.45 (br, 2 H); cod methylene δ 2.30 (br, 4 H), 1.70 (br, 4 H).

Synthesis of *p*-$(N{\equiv}C)C_6F_4N{=}PPh_2CH_2PPh_2$ (5). To a solution of **1** (5.123 g, 10.80 mmol) in dry toluene (100 mL) was injected pentafluorobenzonitrile (3.126 g, 16.20 mmol) by using a syringe. The reaction mixture was refluxed for 12 h before the solvent was removed in vacuo to leave a pale yellow solid. The crude product **5** was crystallized from acetonitrile to obtain pure **5** (yield 5.59 g, 89%; pale yellow needle-shaped crystals; mp 188 °C). Anal. Calcd for $C_{32}H_{22}F_4N_2P_2$: C, 67.10; H, 3.84; N, 4.89. Found: C, 67.13; H, 3.81; N, 4.87. MS (EI, *m/z*): 572 (M^+). ^1H NMR ($CDCl_3$): δ 7.27, 7.60, 7.85 (m, 20 H); PCH_2P methylene δ 3.15 (dd, 2 H, $^2J_{P^{V}H}$ = 12.50, $^2J_{P^{III}H}$ = 1.15 Hz). ^{19}F NMR ($CDCl_3$): AA′BB′ spin system δ −99.85 (m, 2 F), −159.25 (m, 2 F).

Synthesis of *p*-$NC_5F_4N{=}PPh_2CH_2PPh_2$ (6). To a solution of **1** (4.532 g, 9.62 mmol) in dry toluene (100 mL) was injected pentafluoropyridine (2.439 g, 14.40 mmol) by using a syringe. The reaction mixture was refluxed for 20 h before the solvent was removed in vacuo to leave a transparent orange crystalline solid. This crude product was crystallized from acetonitrile to obtain pure **6** (yield 4.95 g, 94%; orange cubic crystals; mp 60 °C). Anal. Calcd for $C_{30}H_{22}F_4N_2P_2$: C, 65.69; H, 4.01; N, 5.10. Found: C, 65.66; H, 4.10; N, 5.08. MS (EI, *m/z*): 548 (M^+). ^1H NMR ($CDCl_3$): δ 7.25, 7.62, 7.87 (m, 20 H); PCH_2P methylene δ 3.17 (dd, 2 H, $^2J_{P^{V}H}$ = 12.65, $^2J_{P^{III}H}$ = 1.15 Hz). ^{19}F NMR ($CDCl_3$): AA′BB′ spin system δ −141.43 (m, 2 F), −155.07 (m, 2 F).

Synthesis of *p*-$(N{\equiv}C)C_6F_4\overline{N{=}PPh_2CH_2PPh_2Rh}(CO)Cl$ (7). A solution of **5** (0.145 g, 0.25 mmol) in dry dichloromethane (25 mL) was added dropwise at 25 °C to a solution of $[Rh(CO)_2Cl]_2$ (0.049 g, 0.12 mmol) also in the same solvent (25 mL). The mixture was stirred at the same temperature for 4 h before the solvent was removed in vacuo to yield an analytically pure brown crystaline solid of **7** as a dichloromethane solvate (yield, after washing with hexane (5 mL), 0.18 g, 90%; brown microcrystalline; mp 215 °C dec). Anal. Calcd for $C_{34}H_{24}Cl_3F_4N_2OP_2Rh$: C, 49.55; H, 2.91; N, 3.40; Cl, 12.91. Found: C, 49.53; H, 2.89; N, 3.38; Cl, 12.90. ^1H NMR ($CDCl_3$): phenyl rings δ 7.27, 7.65, 7.90 (m, 20 H); PCH_2P methylene δ 3.78 (dd, 2 H, $^2J_{HP}$ = 12.0, 8.20 Hz). ^{19}F NMR ($CDCl_3$): AA′BB′ spin system δ −137.27 (m, 2 F), −142.56 (m, 2 F).

Synthesis of *p*-$NC_5H_4\overline{N{=}PPh_2CH_2PPh_2Rh}(CO)Cl$ (8). The reaction of **6** with $[Rh(CO)_2Cl]_2$ was carried out under similar experimental conditions to those described for **7** to obtain the dichloromethane solvate of **8** in 88% yield (yellow microcrystalline; mp 180 °C dec). Anal. Calcd for $C_{32}H_{24}Cl_3F_4N_2OP_2Rh$: C, 48.04; H, 1.25; N, 3.50. Found: C, 48.11; H, 1.21; N, 3.47. ^1H NMR ($CDCl_3$): phenyl rings δ 7.26, 7.60, 7.88 (m, 20 H); PCH_2P methylene δ 3.75 (dd, 2 H, $^2J_{HP}$ = 12.10, 7.50 Hz). ^{19}F NMR ($CDCl_3$): AA′BB′ spin system δ −138.15 (m, 2 F), −147.50 (m, 2 F).

Synthesis of $Me_3SiN{=}PPh_2(CH_2)_2AsPh_2$ (9). A solution of Me_3SiN_3 (2.25 g, 19.64 mmol) in toluene (25 mL) was added dropwise at room temperature to a solution of $Ph_2P(CH_2)_2AsPh_2$ (7.55 g, 17.08 mmol) also in toluene (100 mL). The mixture was heated under reflux for 16 h before the solvent was removed in vacuo to yield an off-white crystalline solid which was recrystallized from dry acetonitrile to obtain pure **8** (yield 8.75 g, 96%; mp 131 °C). Anal. Calcd for $C_{29}H_{33}NAsPSi$: C, 65.79; H, 6.23; N, 2.64. Found: C, 65.76; H, 6.19; N, 2.63. MS (EI, *m/z*): 528 (M^+). ^{31}P NMR (161.93 MHz in $CDCl_3$, vs 85% H_3PO_4): σ_P 1.83 ppm. ^{29}Si NMR (INEPT; 79.5 MHz in $CDCl_3$, vs Me_4Si): δ −11.33 (d, $^2J(^{29}Si–^{31}P)$ = 19.57 Hz).

Synthesis of Arsenic Complexes and Compounds. (a) $Me_3Si\overline{N{=}PPh_2(CH_2)_2AsPh_2Rh}(CO)Cl$ (10). A solution of **9** (0.310 g, 0.58 mmol) in dry dichloromethane (50 mL) was added dropwise (20 min) to a solution of $[Rh(CO)_2Cl]_2$ (0.113 g, 0.29

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mmol) also in the same solvent. The reaction mixture was stirred at 25 °C for 2 h before the solvent was removed in vacuo to yield an analytically pure dichloromethane solvate of **10** (yield, after washing with hexane (5 mL), 0.43 g, 95%; yellow microcrystalline; mp 165 °C dec). Anal. Calcd for $C_{31}H_{35}Cl_3NOAsPRhSi$: C, 47.68; H, 4.48; N, 1.79; Cl, 13.63. Found: C, 47.65; H, 4.46; N, 1.77; Cl, 13.60. ^1H NMR ($CDCl_3$): phenyl rings δ 7.35, 7.55, 7.70 (m, 20 H); AsCH_2CH_2P δ 2.17 (m, 2 H), 2.60 (m, 2 H); $Si(CH_3)_3$ δ 0.05 (s, 9 H). ^{29}Si NMR (INEPT; $CDCl_3$): δ 6.20 (d, 1 Si, $^2J_{PVSi}$ = 5.50 Hz).

(b) The Metallacycles $\overline{\mathbf{N{=}PPh_2(CH_2)_2AsPh_2Rh}}$(cod) (11) and $\overline{\mathbf{N{=}PPh_2(CH_2)_2AsPh_2Ir}}$(cod) (12) were prepared by employing similar experimental conditions to those described above for **10**.

11·CH_2Cl_2: yield 82%; yellow microcrystalline; mp 170 °C dec. Anal. Calcd for $C_{35}H_{38}Cl_2NAsPRh$: C, 55.87; H, 5.05; N, 1.86; Cl, 9.43. Found: C, 55.85; H, 5.01; N, 1.84; Cl, 9.49. ^1H NMR ($CDCl_3$) phenyl rings δ 7.37, 7.60, 7.80 (m, 20 H); AsCH_2CH_2P δ 2.25 (m, 2 H), δ 2.65 (m, 2 H); cod olefinic δ 5.30 (br, 2 H), 5.45 (br, 2 H); cod methylene δ 2.30 (br, 4 H), 1.70 (br, 4 H).

12·CH_2Cl_2: yield 85%; brown microcrystalline; mp 190 °C dec. Anal. Calcd for $C_{35}H_{38}Cl_2NAsPIr$: C, 49.93; H, 4.52;, N, 1.66; Cl, 8.43. Found: C, 50.01; H, 4.49; N, 1.65; Cl, 8.46. ^1H NMR ($CDCl_3$): phenyl rings δ 7.35, 7.62, 7.85 (m, 20 H); AsCH_2CH_2P δ 2.19 (m, 2 H), 2.60 (m, 2 H); cod olefinic δ 5.32 (br, 2 H), 5.40 (br, 2 H); cod methylene δ 2.30 (br, 4 H), 1.72 (br, 4 H).

Reactions of $Ph_3P{=}NSiMe_3$ (15) or $(Me_3SiN{=}PPh_2)_2CH_2$ (16) with $[M(cod)Cl]_2$ (M = Rh or Ir). The reactions were carried out under similar experimental conditions as described for **4** using equimolar quantities of **15** or **16** and $[M(cod)Cl]_2$ (M = Rh or Ir). The spectroscopic (^{31}P NMR) analysis of the reaction mixture clearly showed that no reaction had occurred, and the unreacted phosphoranes **15** and **16** were recovered almost quantitatively.

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Registry No. **1**, 116467-64-2; **2**, 121498-15-5; **3**, 121498-16-6; **4**, 121498-17-7; **5**, 121524-38-7; **6**, 121498-14-4; **7**, 121524-39-8; **8**, 121498-21-3; **9**, 121445-48-5; **10**, 121498-18-8; **11**, 121498-19-9; **12**, 121498-20-2; **13**, 116563-61-2; **14**, 116563-62-3; **15**, 13892-06-3; **16**, 53380-82-8; $W(CO)_6$, 14040-11-0; $Mo(CO)_4(pip)_2$, 59967-36-1; $[Ir(cod)Cl]_2$, 12112-67-3; $[Rh(CO)_2Cl]_2$, 14523-22-9; Me_3SiN_3, 4648-54-8; $Ph_2P(CH_2)_2AsPh_2$, 23582-06-1; $[Rh(cod)Cl]_2$, 12092-47-6; pentafluorobenzonitrile, 773-82-0; pentafluoropyridine, 700-16-3.

Early–Late Transition Metal Bonds: Ruthenium–Titanium Compounds with Aryloxide Ligands

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$[RuH(CO)_2(Cp)]$ reacts with $[Ti(2,6\text{-}Me_2C_6H_3O)(NMe_2)_3]$ (1) and $[Ti(2,6\text{-}Me_2C_6H_3O)_2(NMe_2)_2]$ (2) to produce $[(NMe_2)_2(2,6\text{-}Me_2C_6H_3O)TiRu(CO)_2(Cp)]$ (3) and $[(NMe_2)(2,6\text{-}Me_2C_6H_3O)_2TiRu(CO)_2(Cp)]$ (4), respectively. Both products were characterized spectroscopically, and the structure of 4 was determined by an X-ray diffraction study. Compound 4 crystallizes in the space group $P2_1/n$ with a = 8.201 (3) Å, b = 18.776 (4) Å, c = 16.739 (6) Å, β = 103.90 (3)°, and V = 2526.29 Å^3. Full-matrix least-squares refinement converged at R = 5.6% and R_w = 6.5%. There is a direct, unbridged bond between titanium and ruthenium in 4, with a metal–metal bond length of 2.573 (1) Å. Despite steric crowding in 4, this Ru–Ti distance is 0.09 Å shorter than the Ru–Ti distance in $[(NMe_2)_3TiRu(CO)_2(Cp)]$, attributed in part to the weaker electron-donor ability of aryloxides.

Heterometallic compounds incorporating both early and late transition metals are of current interest due to their relationship to heterogeneous Fischer–Tropsch catalysts. Most of these catalysts consist of low-valent late transition metals supported on high-valent, electropositive metal or nonmetal oxides. The degree of interaction between the metal and its support has profound effects on the activity of the resulting catalyst. The term "strong metal-support interaction" (SMSI) was first used to describe the drastic decreases in the ability of noble metals of periodic groups 8–10 to chemisorb hydrogen when they are supported on titanium oxide. Later, the term was extended to cover a wider range of physicochemical effects on late transition metals supported on early-transition-metal oxides.[1] Indeed, the selectivity of Fischer–Tropsch catalysts for production of hydrocarbons, methanol, or C_2 and higher oxygenates is largely determined by the extent of interaction between the "active" metal and its promoters and/or support.[2] These effects are especially pronounced for noble metals on titanium, zirconium, vanadium, niobium, manganese, and lanthanum oxides. Tauster has recently suggested that SMSI effects result from *direct* interactions of reduced titanium ions (Ti^{3+}) in the support with the group 8–10 metals. This proposal is consistent with extended X-ray absorption fine structure (EXAFS) analysis of rhodium–titania catalysts and other spectroscopic data.[1a]

We are interested in preparing compounds which contain an early transition metal surrounded by "hard", π-donor ligands directly bound to a late transition metal surrounded by "soft", π-acceptor ligands, as models for catalysts which display SMSI. Heterometallic compounds have been the subject of several recent reviews, and it is evident that the majority of the transition-metal compounds contain bonds between low-valent late transition

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