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Preparation, Characterization, and Reactivity of the Early-Transition-Metal/Late-Transition-Metal Heterobimetallic Complexes $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2ML_n$ (M = Ni, Pd, Pt)

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The compound $(C_5H_5)_2Zr(PPh_2)_2$ (**1**) is shown to be capable of acting as a "metallo ligand" in the preparation of early-transition-metal/late-transition-metal heterobimetallic compounds. The chemistry of the resulting species is investigated. **1** reacts with $M(PPh_3)_4$ to yield $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2MPPh_3$ (M = Ni (**2**), Pd (**3**), Pt (**4**)). Reaction of **1** with $(Ph_3P)_2M(CO)_2$ (M = Ni, Pt) gave $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2Ni(CO)_2$ (**5**) and **4**, respectively. Substitution reactions in which basic phosphines (Et_3P, Cy_3P), the activated acetylene $CH_3CO_2C{\equiv}CCO_2CH_3$, CS_2, or PhNCS replaces the Ph_3P of **4** were studied and the products characterized. Substitution reactions with less activated acetylenes (R = H; R′ = Ph, CO_2CH_3) were accomplished by precipitation of Ph_3P as the methylphosphonium salt, which was achieved by addition of CH_3I to the reaction mixture. Attempts to effect oxidative addition on **4** by reaction with CH_3I or $(CH_3)_3O^+BF_4^-$ were unsuccessful. The moderation of the chemical reactivity of the Pt site of **4** by the proximity of the Zr atom may result from the presence of a metal-metal interaction. The evidence for and the nature, degree, and ramifications of such an interaction are discussed.

Introduction

A large number of heterobimetallic complexes have been prepared and characterized;[1-21] however, few contain widely diverse transition metals.[22-26] The combination of both an oxophilic (group 4) metal and a metal from group 9 or 10 presents the possibility for a cooperative activation of a small molecule substrate like CO. Clearly for such cooperation the early and late transition metals must be in close proximity. We have recently reported synthetic routes to complexes in which close proximity of an early and a late transition metal has been achieved.[19,22,25] In this paper we report the synthesis and characterization of complexes that contain Zr and one of Ni, Pd, or Pt. The group 4 and group 10 metals in these compounds are linked by two phosphido bridges. A variety of ligand-substitution and oxidative-addition reactions of the Zr-Pt species are studied. The effect of the proximity of a Zr atom on the chemistry of the Pt site is discussed, and the implications regarding the presence and nature of a metal-metal interaction are considered.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free N_2. Solvents were reagent grade, distilled from the appropriate drying agents under N_2, and degassed by the freeze-thaw method at least three times prior to use. ^1H NMR spectra were recorded on a General Electric QE-300 spectrometer located at Wayne State University using $Si(CH_3)_4$ as the reference. ^{31}P NMR spectra were recorded on a General Electric GN-300 spectrometer located at Wayne State University operating at 121.5 MHz with broad-band proton decoupling. Samples were sealed in 5- or 10-mm tubes under an N_2 atmosphere. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4. Infrared data were recorded on a Nicolet FTIR-5DX spectrometer. Combustion analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. $(C_5H_5)_2Zr(PPh_2)_2$,[27,28] $Ni(PPh_3)_4$,[29] $Pd(PPh_3)_4$,[30] $Pt(PPh_3)_4$,[31] $(Ph_3P)_2Pt(CO)_2$,[32] and $(Ph_3P)_2Ni(CO)_2$[33] were all prepared by literature methods. Dimethyl acetylenedicarboxylate, methyl propiolate, phenylacetylene, and phenyl isothiocyanate were purchased from Aldrich Chemical Co.

Preparation of $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2MPPh_3$ (M = Ni (2), Pd (3), Pt (4)). A 100-mg sample of **1** was dissolved in 25 mL of THF. A stoichiometric amount of the appropriate $M(PPh_3)_4$ was added, and the mixture was allowed to stir overnight. The solution was concentrated to 5 mL, and addition of 20 mL of *n*-hexane resulted in the precipitation of the desired product. The product was isolated by filtration. Washing with three 5-mL portions of *n*-hexane gave 80 mg (52%) of the red-brown Ni-Zr complex **2**, 118 mg (73%) of the yellow-green Pd-Zr complex **3**, and 150 mg (85%) of the yellow-orange Pt-Zr complex **4**. An alternate route for the preparation of **4** is the reaction of **1** with an equimolar amount of $(Ph_3P)_2Pt(CO)_2$ in THF. Isolation of the product is similar to that described above (yield 72%). **2**: ^1H NMR (C_6D_6) δ 7.7-7.0 (m, 35 H), 5.14 (s, 10 H); $^{31}P\{^1H\}$ NMR (THF) δ 106.3 (s, 2 P), 32.9 (s, 1 P). **3**: ^1H NMR (C_6D_6) δ 7.7-7.0 (m, 35 H), 5.04 (s, 10 H); $^{31}P\{^1H\}$ NMR (THF) δ 122.0 (d, 2 P), 28.4 (t, 1 P) ($|J_{P-P}|$ = 17.3 Hz). Anal.

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Calcd for $C_{52}H_{45}P_3ZrPd$: C, 65.03; H, 4.72. Found: C, 64.91; H, 4.87. **4**: ^1H NMR (C_6D_6) δ 7.8–6.9 (m, 35 H), 5.14 (s, 10 H); $^{31}P\{^1H\}$ NMR (THF) δ 122.3 (s, 2 P, $|J_{Pt-P}| = 2680$ Hz), 50.5 (s, 1 P, $|J_{Pt-P}| = 3883$ Hz). Anal. Calcd for $C_{52}H_{45}P_3ZrPt$: C, 59.53; H, 4.32. Found: C, 59.12; H, 4.41.

Preparation of $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2Ni(CO)_2$ (5). A 100-mg sample of **1** was dissolved in 10 mL of benzene. This solution was slowly added to a stirring benzene solution (15 mL) containing 108 mg of $(Ph_3P)_2Ni(CO)_2$. The solution was allowed to stir overnight and the solvent was removed under reduced pressure to a volume of 5 mL. Addition of 10 mL of *n*-hexane resulted in the precipitation of 105 mg (88%) of an orange product **5**·$1.5C_6H_6$ which was washed with three 5-mL portions of *n*-hexane: ^1H NMR (C_6D_6) δ 7.6–7.1 (m, 29 H), 5.14 (s, 10 H); $^{31}P\{^1H\}$ NMR (THF) δ 163.6 (s). Anal. Calcd for $C_{45}H_{39}P_2O_2ZrNi$: C, 65.60; H, 4.77. Found: C, 65.92; H, 4.90.

Reaction of 4 with PR_3, Yielding $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2PtL$ (L = PEt_3 (6), PCy_3 (7)). A 100-mg sample of **4** was dissolved in 5 mL of THF. A stoichiometric amount of the appropriate phosphine was added, and the resulting solution was stirred for 1 h. Addition of 10 mL of *n*-hexane resulted in the precipitation of an orange-yellow solid that was found to contain a mixture of the starting material **4** and the substituted phosphine complex **6** or **7**. Equilibrium constants were determined by integration. **6**: $^{31}P\{^1H\}$ NMR (THF) δ 132.8 (s, 2 P, $|J_{Pt-P}| = 2712$ Hz), 36.9 (s, 1 P, $|J_{Pt-P}| = 3942$ Hz). **7**: $^{31}P\{^1H\}$ NMR (THF) δ 125.1 (s, 2 P, $|J_{Pt-P}| = 2773$ Hz), 38.0 (s, 1 P, $|J_{Pt-P}| = 3530$ Hz).

Preparation of $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2Pt(CH_3CO_2C{\equiv}CCO_2CH_3)$ (8). A 100-mg sample of **4** was dissolved in 20 mL of THF. A stoichiometric amount of dimethyl acetylenedicarboxylate was added, and the mixture was allowed to stir for 3 h. The solvent was removed under reduced pressure to a volume of 5 mL. Addition of 10 mL of *n*-hexane resulted in the precipitation of an orange solid (72 mg, 81%), which was washed with three 5-mL portions of *n*-hexane and dried in vacuo: ^1H NMR (C_6D_6) δ 7.0–7.7 (m, 20 H), 5.00 (s, 10 H), 3.19 (s, 6 H); $^{31}P\{^1H\}$ NMR (THF) δ 137.2 (d, 1 P, $|J_{Pt-P}| = 2195$ Hz); IR (KBr) 1758 (C≡C stretch), 1685 cm^{-1} (C═O stretch). Anal. Calcd for $C_{40}H_{36}P_2O_4ZrPt$: C, 51.72; H, 3.91. Found: C, 51.90; H, 4.30.

Preparation of $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2Pt(CH_3CO_2C{\equiv}CH)$ (9). A 100-mg sample of **4** was dissolved in 20 mL of THF. A stoichiometric amount of the acetylene was added, and the mixture was allowed to stir for 3 h. Addition of a slight molar excess of CH_3I reacted with the liberated triphenylphosphine yielding PPh_3MeI, which precipitated from solution. The phosphonium salt was filtered off, and the solvent was removed under reduced pressure to a volume of 5 mL. Addition of 10 mL of *n*-hexane resulted in the precipitation of an orange-yellow solid (61 mg, 73%). **9**: ^1H NMR (CD_3CN) δ 7.2–7.8 (m, 20 H), 5.08 (s, 10 H), 3.54 (s, 3 H, $|J_{Pt-H}| = 9$ Hz), 3.65 (s, 1 H, $|J_{Pt-H}| = 31$ Hz); $^{31}P\{^1H\}$ (THF) δ 139.7 (d, 1 P, $|J_{Pt-P}| = 2218$ Hz), 134.2 (d, 1 P, $|J_{Pt-P}| = 2291$ Hz) ($|J_{P-P}| = 41$ Hz); IR (KBr) 1744 (C≡C stretch), 1673 cm^{-1} (C═O stretch). Anal. Calcd for $C_{38}H_{34}P_2O_2ZrPt$: C, 52.41; H, 3.93. Found: C, 52.70; H, 4.17.

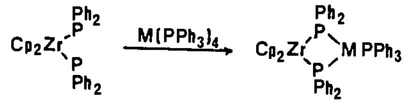
Reaction of 4 with PhC≡CH, Yielding $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2Pt(PhC{\equiv}CH)$ (10). A 100-mg sample of **4** was dissolved in 20 mL of THF. A stoichiometric amount of phenylacetylene was added, and the mixture was allowed to stir overnight. The reaction was monitored by $^{31}P\{^1H\}$ NMR and was found to contain approximately 5% of **10**. A slight excess of CH_3I was added, yielding PPh_3MeI and **10**. The phosphonium salt was filtered off and the product (**10**) precipitated with *n*-hexane: ^1H NMR (CD_3CN) δ 7.8–7.0 (m, 26 H), 5.10 (s, 10 H), 3.27 (s, 1 H); $^{31}P\{^1H\}$ NMR (THF) δ 142.6 ($|J_{Pt-P}| = 2164$ Hz), 135.0 ($|J_{Pt-P}| = 2357$ Hz) ($|J_{P-P}| = 49$ Hz); IR (KBr) 1690 cm^{-1} (C═C stretch).

Preparation of $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2PtCS_2$ (11). A 100-mg sample of **4** was dissolved in 10 mL of benzene. A slight molar excess of CS_2 was added, and the solution was allowed to stand for 1 h, after which time an orange-red crystalline product precipitated. The product was washed with several portions of diethyl ether resulting in an almost quantitative yield (99%) of **11**: ^1H NMR ($(CD_3)_2SO$) δ 7.2–7.8 (m, 20 H), 5.27 (s, 10 H); $^{31}P\{^1H\}$ NMR (DMF) δ 136.3 (d, 1 P, $|J_{Pt-P}| = 1469$ Hz), 111.7 (d, 1 P, $|J_{Pt-P}| = 2702$ Hz) ($|J_{P-P}| = 20$ Hz); IR (KBr) 1142 (C–S stretching), cm^{-1} 699 (C–S bending). Anal. Calcd for $C_{35}H_{30}P_2S_2ZrPt$: C, 48.71; H, 3.50. Found: C, 48.69; H, 3.74.

Reaction of 4 with SCNPh, Yielding $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2Pt(SCNPh)$ (12). A 100-mg sample of **4** was dissolved in 5 mL of THF. A stoichiometric amount of phenyl isothiocyanate was added and stirred for 1 h. Addition of 10 mL of *n*-hexane resulted in the precipitation of the yellow-orange product **12** along with an unidentified side product. Attempts to purify **12** by chromatography were unsuccessful. **12**: $^{31}P\{^1H\}$ NMR (THF) δ 139.8 (d, 1 P, $|J_{Pt-P}| = 1499$ Hz), 114.7 (d, 1 P, $|J_{Pt-P}| = 2581$ Hz) ($|J_{P-P}| = 23$ Hz).

Results and Discussion

Reactions of **1** with $M(PPh_3)_4$ (M = Ni, Pd, Pt) led to the isolation in good yields (50–85%) of red-brown, yellow-green, and yellow-orange solids, respectively. These compounds were air-sensitive. The nickel species **2**, being the least stable, decomposes in the solid state after several days. The instability of other nickel diphenylphosphido-bridged species has been noted by Geoffroy et al.[12] The Pd and Pt compounds were stable both in the solid state and in solution under an inert atmosphere. Analytical and ^1H NMR data were consistent with the formulation of these products as **2**, **3**, and **4**, respectively (eq 1). The $^{31}P\{^1H\}$ NMR spectra of these compounds show two peaks with an intensity ratio of 2:1. The more intense signals occur downfield in the range of 105–122 ppm. These signals arise from the phosphido bridges between Zr and the group 10 metal. The upfield resonances (25–40 ppm) are consistent with coordinated PPh_3. Only the Pd complex **3** showed phosphorus–phosphorus coupling. The expected low-field doublet and high-field triplet were observed with a $|J_{P-P}|$ of 17 Hz. The signals in the spectra of the Ni and Pt compounds **3** and **4** did not exhibit P–P coupling but were broad (75 Hz at half-height) at 298 K. When the compounds were cooled to 198 K, the peaks narrowed (25 Hz at half-height) but no coupling was resolved. The lack of observable coupling suggests that the Zr–P_2–M core may be described as a fluxional "butterfly". A metal–metal interaction across the butterfly would give a pseudotetrahedral geometry to the group 10 metal atom. Similar absences of P–P coupling have been reported for a phosphido-bridged Rh complex where a pseudotetrahedral geometry was confirmed.[34]

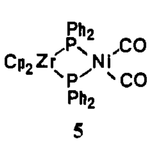


(1)

1

2, M = Ni
3, M = Pd
4, M = Pt

1 reacts with $(Ph_3P)_2M(CO)_2$ (M = Ni, Pt). In the case of the Pt reaction loss of CO and PPh_3 occurs, yielding **4**. The nickel–carbonyl species reacts with **1** to give an orange product in high yield (85–90%). The IR bands at 1941 and 2000 cm^{-1} clearly indicate the presence of terminal carbonyl groups. The singlet in the $^{31}P\{^1H\}$ NMR spectrum occurs at 163.6 ppm, indicating μ-PPh_2 moieties. The analytical and ^1H data are consistent with the formulation of this product as **5**·$1.5C_6H_6$. The benzene of crystallization can be removed by prolonged drying under vacuum. A hafnium analogue of this Zr(IV)–Ni(0) complex (i.e. $Cp_2Hf(\mu\text{-}PEt_2)_2Ni(CO)_2$) has been recently reported by Baker et al.[21]



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Attempts to perform oxidative additions to the Pt(0) end of **4** were studied. Addition of CH_3I or $(CH_3)_3O^+BF_4^-$, even in large excess, had no effect. In general, the products of oxidative additions to Pt(0) species are known to be strongly solvent-dependent; however, reactions of $Pt(PPh_3)_3$ or $Pt(PPh_2CH_3)_3$ with CH_3I or $(CH_3)_3O^+BF_4^-$ are known to proceed under mild conditions.[35] The lack of reactivity of **4** with these reagents clearly demonstrates that the Pt site in **4** does not behave as a typical Pt(0). This

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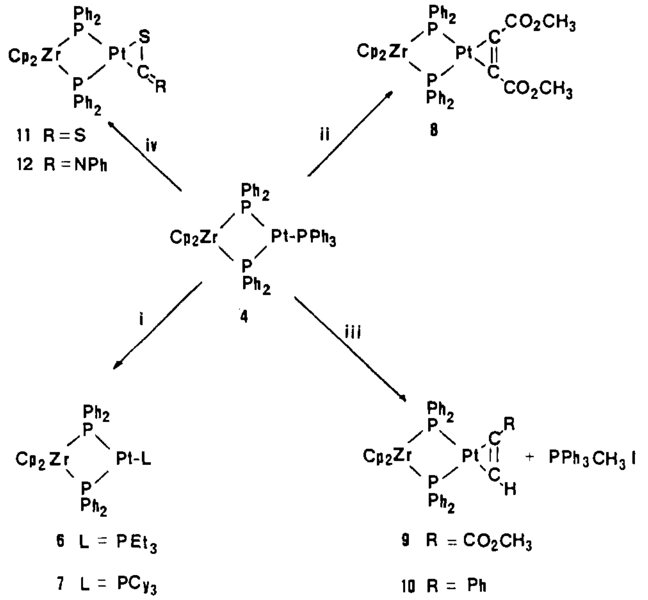

Figure 1. Reactions of 4: (i) PEt$_3$ or PCy$_3$; (ii) CH$_3$CO$_2$C≡CCO$_2$CH$_3$; (iii) CH$_3$CO$_2$C≡CH or PhC≡CH, excess CH$_3$I; (iv) CS$_2$ or SCNPh.

alteration of reactivity presumably arises as a result of the proximity of the Zr atom.

The reactions of **4** with PEt$_3$ and PCy$_3$ were monitored by ^{31}P{^{1}H} NMR. The spectra show established equilibria in which the more basic alkylphosphine exchanges with the PPh$_3$ on the Pt. Thus in these spectra signals arising from the starting material **4**, free PPh$_3$, the free basic phosphine as well as the complexes (C$_5$H$_5$)$_2$Zr(μ-PPh$_2$)$_2$PtL (L = PEt$_3$ (**6**), PCy$_3$ (**7**)) are observed (Figure 1). No P–P coupling was observed in these substituted complexes; however, Pt–P coupling on the order of 2700 Hz for the phosphido phosphorus atoms and 3900 Hz for the coordinated phosphine were seen. Substitution occurred to a greater extent with PEt$_3$ ($K \simeq 3$) than with PCy$_3$ ($K \simeq 0.03$). Clearly, this reflects the relative steric bulk of the two ligands. Attempts to isolate the substituted compounds were impeded by the presence of **4** in solution; thus, no analytical data are available for **6** or **7**.

Reaction of **4** with the activated acetylene, dimethyl acetylenedicarboxylate, led to the isolation of the orange compound **8** (Figure 1). The IR bands at 1758 and 1685 cm^{-1} indicate the presence of coordinated acetylene. Monitoring of the reaction mixture by ^{31}P{^{1}H} NMR showed the signals arising from free PPh$_3$ and the product **8**. The single resonance at 137.2 ppm with Pt satellites ($|J_{\mathrm{Pt-P}}| = 2195$ Hz) as well as the ^{1}H NMR data is consistent with displacement of PPh$_3$ by the acetylene. Similar substitution reactions are known for diphenylphosphido-bridged W–Pt[12] and dicyclohexylphosphido-bridged W–M (M = Ni, Pd, Pt) complexes.[34]

The reactions of less activated acetylenes (RC≡CH (R = CO$_2$CH$_3$, Ph)) with **4** were monitored by ^{31}P{^{1}H} NMR. The spectra showed signals arising from some displaced (i.e. free) PPh$_3$ and some **4** as well as two sets of doublets with Pt satellites in the μ-PPh$_2$ region, which are assigned to the acetylene-substituted products **9** (R = CO$_2$CH$_3$) and **10** (R = Ph) (Figure 1). The inequivalence of the phosphorus atoms in **9** and **10** arises from the asymmetry of the alkyne. The position of the equilibria is dependent on the substituent R. The equilibrium constants (K) are approximately 9.0 and 0.08 for R = CO$_2$CH$_3$ and Ph, respectively. Reaction with these less activated acetylenes, in particular PhC≡CH, is in contrast to the reactions of the group 6/group 10 heterobimetallic complexes where no reaction was observed.[12,36] The equilibria can be displaced toward complete acetylene substitution by addition of CH$_3$I. The CH$_3$I acts as a PPh$_3$ scavenger, forming the phosphonium salt, which precipitates from solution, yielding the acetylene-substituted complexes (Figure 2). In the case of W–Pt bimetallic complexes,[12] PPh$_3$ was removed by using O$_2$. This method was only effective for substitution reactions involving activated acetylenes. Of course, the oxophilicity of Zr in **4** precludes the use of O$_2$ as a phosphine scavenger in the present system.

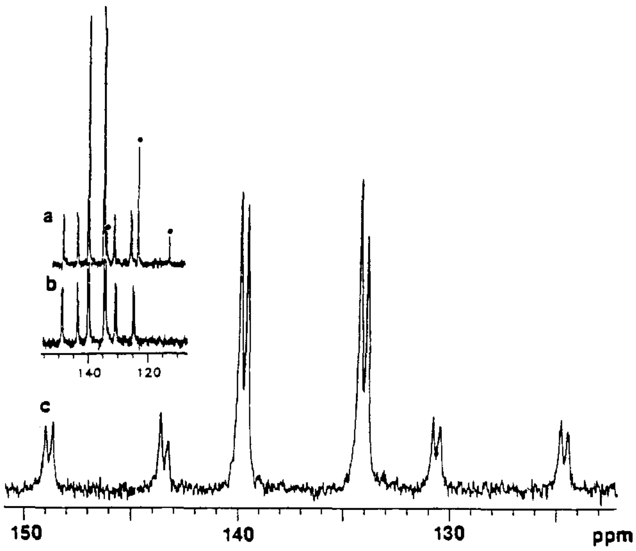

Figure 2. ^{31}P{^{1}H} NMR spectra of the reaction of 4 with CH$_3$CO$_2$C≡CH: (a) spectrum of a 1:1 mixture of 4 and the acetylene, showing resonances from 4 (high field region only, noted by •) and 9 only; (b) the same region after addition of excess CH$_3$I shows only resonances arising from 9; (c) expanded view of (b) showing the resonances and Pt satellites of 9.

Compound **4** reacts with CS$_2$, yielding almost quantitatively a red-orange microcrystalline product. IR data suggest the presence of coordinated CS$_2$. The ^{31}P{^{1}H} NMR spectrum of this product shows two coupled resonances in the μ-PPh$_2$ region, thus suggesting two inequivalent phosphorus atoms. The spectrum also shows a signal arising from displaced PPh$_3$, thus suggesting replacement of the phosphine by CS$_2$. These data along with the analytical and ^{1}H NMR data led to the formulation of the product as **11** (Figure 1). The assignment of the signals in the ^{31}P{^{1}H} NMR spectrum of **11** is not unambiguous. However, the downfield phosphido resonance is assigned to the phosphorus atom trans to the bound sulfur atom on the basis of donor–acceptor arguments.

Reaction of **4** with PhNCS was also examined. At low concentrations of PhNCS the ^{31}P{^{1}H} NMR spectrum of the reaction mixture showed signals arising from **4** and free PPh$_3$ and a new set of two coupled doublets with Pt satellites. These were tentatively assigned to **12**, the PhNCS analogue of **11** (Figure 1). In the presence of a full or greater equivalent of PhNCS the resonances assigned to **12** persist; however, an additional upfield resonance (−20 ppm) with Pt satellites also appears. Attempts to separate these species or crystallize the products have been unsuccessful. A more detailed study of the course of this reaction is in progress.

The existence of a direct Pt–Zr interaction is subject for discussion. Spectroscopic data such as the ^{31}P NMR chemical shifts of the phosphido groups have been shown not to be a reliable means of monitoring the presence or absence of metal–metal bonds in bimetallic systems.[12] Nonetheless, the downfield ^{31}P phosphido resonances in **2**–**12**, as well as the blue shift of the carbonyls of **5** ($\Delta\nu \simeq$ 15–20 cm^{-1}) relative to those of (C$_5$H$_5$)$_2$Th(μ-PPh$_2$)$_2$Ni(CO)$_2$[26] and (C$_5$H$_5$)$_2$Hf(μ-PEt$_2$)$_2$Ni(CO)$_2$,[21] suggest a metal–metal interaction.[20] In the case of **4**, its chemistry also provides some information. The Pt center shows electrophilic reactivity typical of Pt(0) species (i.e. ligand-substitution reactions). However, in reactions where the Pt center is presumed to act as a nucleophile (oxidative additions) the bimetallic **4** shows a marked lack of reactivity compared to monometallic Pt(0) complexes. This alteration in the reactivity of the Pt site is consistent with a

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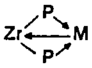
(36) Taylor, H.; Gelmini, L.; Loeb, S. J.; Stephan, D. W., unpublished results.

reduction in the electron density at the Pt center, and thus it is possible that a dative bond between the electron-rich Pt(0) and the electron-deficient Zr(IV) exists. Such an interaction would be comparable to the d^{10}→d^0 dative bond between Cu(I) and Ti(IV) observed in the complex $[Cp_2Ti(SCH_2CH_2PPh_2)_2Cu]BF_4$.[22] In the more closely related complex $(C_5H_5)_2Th(\mu\text{-}PPh_2)_2Ni(CO)_2$,[26] a short Th–Ni distance has been observed crystallographically. The implication of a metal–metal interaction in the Th–Ni species can be extended to the present compounds. Other workers have recently confirmed the presence of metal–metal dative bonds in the related Hf/Pd heterobimetallic complexes by crystallographic methods as well as molecular orbital calculations.[37] Thus it appears that **13** best represents the nature of the metal–phosphorus core of these compounds.



13

The results described herein demonstrate a convenient synthetic route to heterobimetallic complexes in which two widely diverse transition metals are brought into close proximity. The utilization of **1** as a "metallo ligand" allows the preparation of heterobimetallic complexes, providing an alternative to the "bridge-assisted-dianion" approach of Geoffroy.[2,9,12,14–17,20] The unique reactivity patterns that arise from the metal–metal interaction in these complexes are the subject of our current work.

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(37) Baker, R. T., personal communication.

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Factors Influencing Jahn–Teller Distortions in Six-Coordinate Copper(II) and Low-Spin Nickel(II) Complexes

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A simple method of calculating the Jahn–Teller distortions of copper(II) complexes to first order is described, and this is shown to predict ligand displacements generally somewhat smaller than those observed experimentally. The effects of anharmonicity in the vibrational potential, second-order electronic corrections, and d–s mixing on the potential surface are discussed, and the inclusion of these leads to calculated geometries and other Jahn–Teller parameters of typical copper(II) complexes in reasonable agreement with experiment. It is suggested that the electronic and geometric structures of spin-paired nickel(II) complexes may be considered to be derived from a Jahn–Teller distortion of the ^1E_g excited state of a regular octahedral complex. This allows the in-plane bond lengths to be estimated satisfactorily and provides a rationalization of the fact that the axial bonds in such complexes are very long or absent.

Introduction

The role of the Jahn–Teller effect in influencing the molecular geometries and physical properties of transition-metal complexes has become increasingly apparent in recent years.[1–5] Moreover, although the importance of this effect on the structural chemistry of copper(II) has sometimes been queried,[6,7] it is clear that, at least at low temperature, copper(II) complexes almost invariably adopt distorted geometries that are in agreement with the predictions of the Jahn–Teller theorem. At higher temperatures, dynamic fluctuations between the distorted complexes may occur and here again models based upon the Jahn–Teller theorem have been widely used to describe the spectroscopic and X-ray diffraction properties of such systems.[8–11]

Despite the overall success of the theorem some aspects of the stereochemistry of copper(II) complexes still require clarification. In particular, the Jahn–Teller active vibrational mode of an octahedral complex of a d^9 metal ion is doubly degenerate and, to first order, theory suggests not only that a compressed-tetragonal geometry is just as likely as the elongated stereochemistry which is invariably observed experimentally, at least at low temperature, but also that the geometry should oscillate dynamically between these extremes along a normal coordinate corresponding to an orthorhombic molecular symmetry. Several suggestions have been made of ways in which the simple model may be extended to bring it into better agreement with experiment. Öpik and Pryce proposed the addition of an anharmonic term to the vibrational potential,[12] and the importance of this term has also been recognized by Bacci.[13] The extension to second order of the electronic term in the total potential energy expression has been investigated quantitatively both by Ballhausen and Liehr[14] and by Bacci,[13] though this was found to stabilize a compressed rather than an elongated geometry. Finally, a number of research workers have independently suggested that the elongated-tetragonal geometry characteristic of six-coordinate copper(II) complexes results from configuration interaction between the 4s and $3d_{z^2}$ metal orbitals.[15–17]

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