The Facile Preparation of Early Transition Metal/Late Transition Metal Heterobimetallic Complexes; $(\eta^5\text{-}C_5H_5)_2Zr(PPh_2)_2$ as a 'Metalloligand' for Ni, Pd and Pt

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Current interest in heterobimetallic complexes stems from the potential of such species for the enhanced activation of small molecule substrates [1–24]. Bimetallic complexes that incorporate early oxophilic metals such as Ti or Zr as well as a group 10 transition metal are of particular interest from the perspective of catalyst development and yet few such compounds are known [21–24]. Herein we describe a new and convenient route for the synthesis of a variety of complexes containing both the group 4 metal Zr and one of the group 10** metals Ni, Pd, or Pt. The methods described demonstrate the utility of the complex $(\eta^5\text{-}C_5H_5)_2Zr(PPh_2)_2$ (**1**) as a 'metalloligand' in the synthesis of early transition metal/late transition metal heterobimetallic compounds.

Initial attempts to displace PhCN from $(PhCN)_2PtCl_2$ using (**1**) led to the isolation of two species; an intractable yellow solid and colorless crystals. IR spectroscopy and melting point confirmed that the colorless material was $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (**2**). It is apparent that disproportionation occurred yielding (**2**) and the yellow Pt–phosphide polymer (**3**). Similar reactions with main group halides have been described by Wade *et al.* [25].

Disproportionation can be avoided by the exclusion of exchangeable halides from the starting materials. The reaction of (**1**) with $M(PPh_3)_4$ (M = Pt, Ni, Pd) led to the isolation in good yield (50–85%) of the yellow–orange, red–brown and orange compounds (**4**), (**6**) and (**7**) respectively. Analytical and ^1H NMR data were consistent with the formulations of these products†. The $^{31}P\{^1H\}$ NMR spectra in each case show two peaks with an integrated intensity ratio of 2:1. The presence of the downfield resonances in vicinity of 105–122 ppm suggests phosphido-bridges between Zr and the group 10 metal. Similar shifts have been observed for related group 4-group 6 phosphido-bridged species [12, 20, 21]. The upfield resonances (25–50 ppm) are indicative of coordinated phosphine. No phosphorus–phosporus coupling is observed in these spectra however the peaks are broad at room temperature (75 Hz at half-height). On cooling to −100 °C the peaks do narrow (25 Hz at half-height) but no phosphorus–phosphorus coupling is revealed. This suggests a fluxional butterfly-type $M{-}P_2{-}M'$ core in which a metal–metal interaction yields a pseudotetrahedral geometry about the group 10 metal atom. Similar absences of P–P coupling have been noted for phosphido-bridged Rh species where a pseudo-tetrahedral geometry has been confirmed crystallography [26].

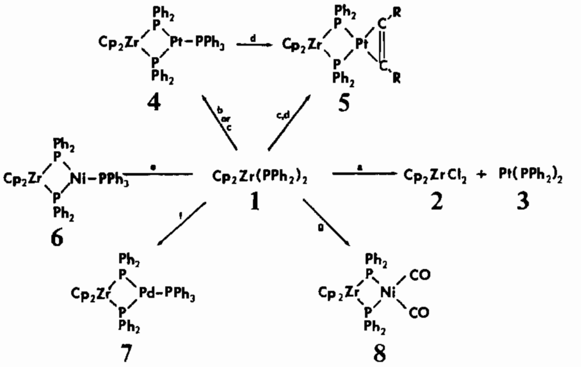

Fig. 1. Reactions of $(\eta^5\text{-}C_5H_5)_2Zr(PPh_2)_2$ as a 'metalloligand'. (a) $(PhCN)_2PtCl_2$, (b) $Pt(PPh_3)_4$, (c) $(Ph_3P)_2Pt(CO)_2$, (d) $CH_3CO^2C{=}CCO_2CH_3$, (e) $Ni(PPh_3)_4$, (f) $Pd(PPh_3)_4$, (g) $(Ph_3P)_2Ni(CO)_2$.

An alternate route to species (**4**) involved the reaction of $(Ph_3P)_2Pt(CO)_2$ with (**1**). In this reaction $^{31}P\{^1H\}$ NMR data clearly showed that the product was identical to that obtained by the route described above. Apparently displacement of CO with concurrent loss of a Ph_3P group occurred yielding (**4**).

Compound (**4**) reacts with dimethylacetylenedicarboxylate (DMADC) yielding the orange product (**5**) quantitatively. The ^1H and $^{31}P\{^1H\}$ NMR spectra of this compound are consistent with the replacement of Ph_3P with DMADC†. The IR absorption at 1758 and 1685 cm^{-1} indicate the presence of the coordinated acetylene. Similar replacement reactions have been described for related Mo(0)–Pd(II) [27] and W(0)–Pt(II) [12] phosphido-bridged species.

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**This notation is in accord with the recent action of IUPAC nomenclature committee.

†See footnote right hand column.

†Spectral and analytical data for: $^{31}P\{^1H\}$ NMR (δ ppm downfield of external 85% H_3PO_4), (**4**): 122.3 J(Pt–P) 2680, 50.5 J(Pt–P) 3883 Hz; (**5**): 137.2; J(Pt–P) 2195 Hz; (**6**): 106.3, 32.9; (**7**): 122.5, 28.9; (**8**): 163.6. ^1H NMR (δ ppm downfield of TMS), (**4**): 7.8–6.9(m), 5.14(s); (**5**): 7.7–7.0(m), 5.00(s), 3.19(s); (**6**): 7.7–7.0(m), 5.14(s); (**7**): 7.7(m), 5.04(s); (**8**): 7.6–7.1(m), 5.14(s). *Anal.* (%) calc. (found) for (**4**): C, 59.53(59.12), H, 4.32(4.41); (**5**): C, 51.72(51.90), H, 3.91(4.30); (**6**): unavailable due to extreme air sensitivity; (**7**): C, 65.03(64.91), H, 4.72(4.87); (**8**): $1.5C_6H_6$: C, 65.60(65.92), H, 4.77(4.90).

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Compound (**1**) reacts with the Ni(0) compound $(Ph_3P)_2$ $Ni(CO)_2$ to give the orange product (**8**) in high yield (85–90%). Solid state IR bands at 1936, 1941 and 2000 cm^{-1} suggest the presence of terminal carbonyl groups. Analytical data, ^{1}H and ^{31}P{^{1}P} NMR spectra are consistent with the formulation (**8**)*. A hafnium analogue of this Zr(IV)–Ni(0) species has been recently prepared by Baker *et al.* [21].

The existence of a metal–metal interaction in these compounds is a subject for speculation. While the downfield shft of the ^{31}P NMR signals of the phosphido groups in the present compounds is, by itself, insufficient evidence for a metal–metal interaction [12], the absence of P–P coupling in (**4**), (**6**) and (**7**) does suggest the possibility. Furthermore we recently described a Cu(I) (d^{1-}) → Ti(IV) (d^{-}) dative bond in a thiolate bridged species [22]. Inasmuch as compounds (**4**), (**5**), (**6**), (**7**) and (**8**) are all d^{1-}–d^{-} bimetallic systems the possibility of an analogous metal–metal interaction exists. Whether or not a metal–metal bond is present, the close proximity of an early transition metal to a late transition metal will undoubtedly lead to unique reactivity patterns. This is the subject of current work.

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*See footnote † p. L17.

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