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Reaction of zirconocene complexes with phosphorous ylides: evidence for the formation of Cp2Zr(C6H5)CHPPh3 from diphenylzirconocene and CH2PPh3 by an aryne mechanism

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plex 4 (Scheme I). An analogous rearrangement is implied along the reaction path to a zirconium-substituted indan formed by the addition of CO to 1,1-bis(η-cyclopentadienyl)-1-zirconaindan.[3e,21]

Upon heating 0.2 M solutions of the methyl and benzyl analogues of complex 2, $Cp_2ZrCH_3[CH(Si(CH_3)_3)SCH_3]$ (5) and $Cp_2ZrCH_2C_6H_5[CH(Si(CH_3)_3)SCH_3]$ (6), at 82 °C for ca. 1 week in $C_6D_5CD_3$, complexes 5 and 6 were found by NMR measurement to be less than 5% decomposed. In a control experiment under similar conditions complexes 5 and 6 were recovered in over 90% yield after 1 week in solution at 82 °C.[22] The greater propensity of complex 2 relative to complexes 5 and 6 to undergo rearrangement to form complex 4 is consistent with the mechanism in Scheme I and can be understood in terms of the greater migratory aptitude of a phenyl group, relative to the methyl and benzyl groups in nucleophilic migrations.[23] The rearrangement of 2 to 4 appears in this respect to reflect the well-known migratory aptitudes of the pinacole rearrangement.[23] To test this idea of a nucleophilic attack of the phenyl group on the α-carbon, the anisole derivative $Cp_2Zr(p\text{-}C_6H_4OCH_3)[CH(Si(CH_3)_3)SCH_3]$ (8)[22] was prepared and subjected to thermolysis as the anisole group is well-known to undergo nucleophilic migration faster than a phenyl group.[23] Complex 8 was found to undergo thermolysis to form $Cp_2ZrSCH_3[CH(Si(CH_3)_3)C_6H_4OCH_3]$ with first-order kinetics five times faster than the analogous rearrangement of complex 2.[22]

The α-thiomethyl group in these complexes not only imparts greater stability to these complexes than has been reported for α-zirconocenyl ethers but also opens up reaction pathways which are not available to other alkylzirconocene and -titanocene complexes bearing simple hydrocarbon ligands.[24]

The novel rearrangement reported here may shed light on another possible reaction pathway in the conversion of CO and H_2 to hydrocarbons. Further work is in progress to investigate this possibility as well as the importance of varying steric and electronic effects on this rearrangement.

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Reaction of Zirconocene Complexes with Phosphorus Ylides: Evidence for the Formation of $Cp_2Zr(C_6H_5)CHPPh_3$ from Diphenylzirconocene and CH_2PPh_3 by an Aryne Mechanism

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Summary: The reactions of methylenetriphenylphosphorane with $[Cp_2Zr(H)Cl]_x$, $Cp_2Zr(CH_3)_2$, and $Cp_2Zr(C_6H_5)_2$ have been studied. At 60 °C methylene transfer from $CH_2{=}PPh_3$ to the hydridozirconocene chloride occurs producing methylzirconocene chloride and triphenylphosphine. In contrast to dimethylzirconocene, which turns out to be unreactive up to 170 °C, diphenylzirconocene at 80 °C reacts with the ylide to form $Cp_2Zr(C_6H_5)CHPPh_3$ (**1c**). This reaction proceeds through an (η^2-aryne)zirconocene intermediate as revealed by a labeling experiment. The $Cp_2Zr(C_6H_5)$-substituted ylide has been characterized by NMR spectra at various temperatures and an X-ray structure analysis. **1c** crystallizes in space group *Pbca* with $a = 10.927$ (1) Å, $b = 17.998$ (3) Å, $c = 28.992$ (2) Å, and $Z = 8$. The preferred conformation and a rather short Zr–C7 bond distance (2.157 (4) Å) indicate substantial π-interaction of the Zr–C(ylide) linkage.

Although π-conjugation accounts for the wealth of structures and chemical reactivities of organic compounds, it has been considered less important in inorganic chemistry.[1] However, conjugative effects in organometallic systems are attracting increasing attention.[2] Many of the unique stereoelectronic features observed for organometallic systems of electron-deficient early-transition-metal centers are caused by π-interaction across a rigid σ-framework. For example, partial multiple-bond character has been demonstrated both structurally and chemically for molecules involving Cp_2Zr–C, –O, –N, or –P linkages.[3]

Zirconocene-substituted ylides $Cp_2Zr(X)CHPPh_3$ (1) are most interesting substrates in this regard. $Cp_2Zr(Cl)CHPPh_3$ (**1a**) has been shown to exhibit a substantial Zr–C(ylide) double-bond character (bond distance = 2.15 Å; rotational barrier $\Delta G^{\ddagger}_{-95\,°C} = 8.6$ kcal/mol).[4]

1a has been prepared by the slow reaction of Cp_2ZrCl_2 with a large excess of methylenetriphenylphosphorane (2), the ylide serving as both a nucleophile and a base in subsequent second-order reaction steps.[4] In an attempt to improve this interesting synthetic sequence, we tried to change the intermolecular second reaction step into an intramolecular hydrogen abstraction from the ylide carbon atom. We had hoped to obtain the $Cp_2Zr(X)$-substituted ylides **1a–c** (X = Cl, CH_3, C_6H_5) by the reaction of $CH_2{=}PPh_3$ with $[Cp_2Zr(H)Cl]_x$ (3), $Cp_2Zr(CH_3)_2$ (4), or $Cp_2Zr(C_6H_5)_2$ (5) and subsequent elimination of H_2, methane, or benzene, respectively. This led to the unexpected discovery of a new reaction type leading to **1c**.

Hydridozirconocene chloride (3) does not react with 2 via an ylide addition/hydrogen abstraction reaction sequence. Instead a clean methylene-transfer reaction is observed at 60 °C, producing methylzirconocene chloride (7)[5] and triphenylphosphine in high yield. Apparently, by

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[1] See, however: Chisholm, M. H. *Transition Met. Chem.* (Weinheim, Ger.) 1978, *3*, 321.

[2] See, e.g.: Herrmann, W. A.; Weichmann, J.; Küsthardt, U.; Schäfer, A.; Hörlein, R.; Hecht, C.; Voss, E.; Serrano, R. *Angew. Chem.* 1983, *95*, 1019. Herrmann, W. A.; Hecht, C.; Ziegler, M. L.; Balbach, B. *J. Chem. Soc., Chem. Commun.* 1984, 686. Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. "Transition Metal Carbene Complexes"; Verlag Chemie: Weinheim, 1983.

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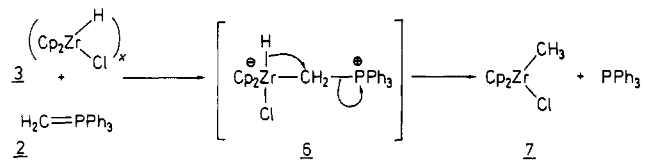
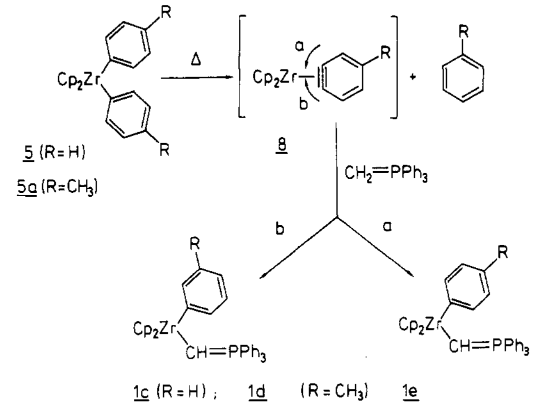
Scheme I



Scheme II



far the favored reaction of the intermediate ylide addition product **6** is a 1,2-hydrogen migration from zirconium to carbon with displacement of the good PPh_3 leaving group (Scheme I). This interesting methylene-transfer reaction[6] could not be developed into a CC coupling reaction. Even when heated to 170 °C for 3 h, dimethylzirconocene (**4**) turned out to be completely unreactive toward methylenetriphenylphosphorane (**2**). Above this temperature unspecific decomposition took place.

In contrast, CH_2PPh_3 (**2**) reacts cleanly with diphenylzirconocene (**5**) at 80 °C to form the zirconium-substituted ylide $Cp_2Zr(C_6H_5)CHPPh_3$ (**1c**). This is probably by far the best synthetic procedure for the formation of a derivative of complex **1**. Starting from a 1:1 mixture of **2** and **5** the reaction at 80 °C in heptane solution goes almost to completion within a period of 5 h. **1c** is formed practically free of side products and has been isolated in >90% yield.[7]

1c exhibits chemical and structural features similar to those reported for **1a**. Restricted rotation of the $Cp_2Zr–CH$ moiety is revealed by dynamic NMR spectroscopy ($\Delta G^{\ddagger}_{-102\,°C} = 8.4 \pm 0.3$ kcal/mol).[8] Partial multiple-bond character of the Zr–C (ylide) linkage is also inferred from the X-ray structure analysis.[9] The preferred conformation and the rather short Zr–C7 bond distance (2.157 (4) Å) indicate a pronounced carbon–zirconium π-interaction (see Figure 1).

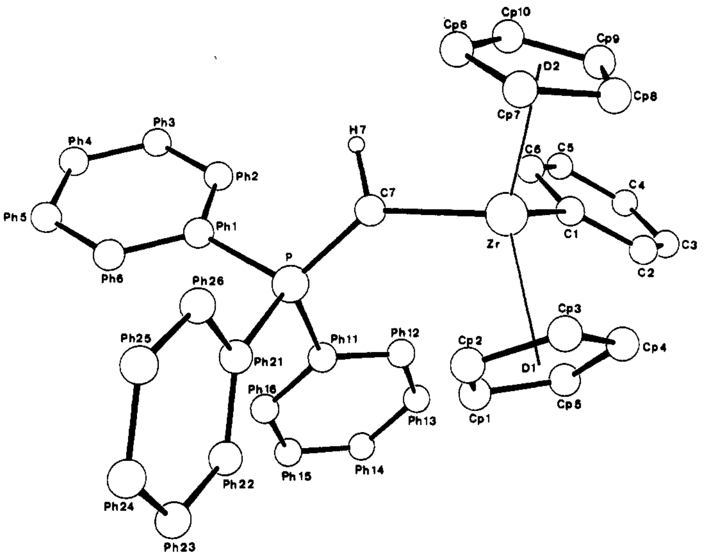


Figure 1. Molecular structure of $Zr(C_6H_5)(\eta\text{-}C_5H_5)_2[CH{=}P(C_6H_5)_3]$ showing the atom numbering scheme. Selected distances (Å) and angles (deg) (esd in parantheses): Zr–C1 = 2.338 (5); Zr–D1 = 2.254; Zr–D2 = 2.238; Zr–C7 = 2.157 (4); D1–Zr–D$_2$ = 130.1; C1–Zr–C7 = 98.0 (2); Zr–C7–P = 137.7 (2); P–C7 = 1.689 (4); average C7–P–Ph = 115 (1); average Ph–P–Ph = 104 (3). D1 and D2 are the midpoints of the cyclopentadienyl rings.

The composition of the educts and products are consistent with **1c** being formed by a straightforward abstraction of a hydrogen atom from the ylide carbon in an intermediate $Cp_2ZrPh_2/CH_2{=}PPh_3$ addition product (analogous to **6**) by one of the zirconium-bound phenyl groups serving as an internal base. However, there is convincing evidence that the $Cp_2Zr(C_6H_5)CHPPh_3$ obtained was not produced in this manner but via an (η^2-1,2-didehydrobenzene)$ZrCp_2$ intermediate (**8**).[10] The intermediacy of the (aryne)zirconocene has been established by a classical experiment.[11] Thermolysis of di-*p*-tolylzirconocene (**5a**) should lead to the unsymmetrically substituted (aryne)$ZrCp_2$ complex (**8a**, methyl at C4).[10a] Subsequent addition of the ylide **2** can occur from either side a or b to give two differently substituted Cp_2Zr(tolyl) ylides after intramolecular hydrogen transfer. Indeed, these products **1d** and **1e** were obtained in a 60:40 ratio

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(5) The isolated **7** (60% yield) was shown to be identical with the reported $Cp_2Zr(CH_3)Cl$ prepared by a different route: Surtees, J. R. *J. Chem. Soc., Chem. Commun.* **1965**, 567. Anal. Calcd for $C_{11}H_{13}ClZr$ (271.9): C, 48.59; H, 4.82. Found: C, 48.79; H, 4.81. ^{1}H NMR (C_6D_6): δ 5.75 (s, 10 H, Cp), 0.42 (s, 3 H, CH_3). MS: *m/e* 255 ($M^+ - CH_3$).

(6) For various CH_2-transfer reactions of ylides see, e.g: Fiederling, K.; Grob, I.; Malisch, W. *J. Organomet. Chem.* **1983**, *255*, 299. Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Morris, M. J. *J. Organomet. Chem.* **1981**, *215*, C30. Korswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. *Angew. Chem.* **1981**, *93*, 1073. Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 6543. Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *Ibid.* **1977**, *99*, 2127.

(7) **1c** was prepared by heating a suspension of 3.81 g (10 mmol) of **5** and 2.97 g (11 mmol) of the ylide **2** at 80 °C for 5 h. Subsequent crystallization from the resulting yellow solution yielded **1c** as a yellow microcrystalline solid: 5.20 g (90.7%); mp 130–140 °C dec; ^{1}H NMR (C_6D_6) δ 5.80 (s, 10 H, Cp), 5.65 (d, $^2J_{HP}$ = 12.2 Hz, 1 H, C*H*=P), 7.5–7.96 and 6.90–7.35 (m, 20 H, Ph, PPh_3); ^{31}P{^{1}H}NMR (C_6D_6) δ 16.0; ^{13}C NMR (CD_2Cl_2) (atom numbering according to Figure 1) δ 108.3 (d, $^1J_{CH}$ = 172 Hz, Cp), 106.2 (dd, $^1J_{CH}$ = 117 Hz, $^1J_{CP}$ = 28.2 Hz, ylide-C), 181.7 (s, C1), 142.9 (d, $^1J_{CH}$ = 154 Hz, C2), 125.7 (d, $^1J_{CH}$ = 154 Hz, C3), 123.1 (d, $^1J_{CH}$ = 157 Hz, C4), PPh_3, 134.7 (d, $^1J_{CP}$ = 81.3 Hz), 133.4 (dd, $^1J_{CH}$ = 164 Hz, $^2J_{CP}$ = 9.3 Hz, ortho-C), 128.7 (dd, $^1J_{CH}$ = 163 Hz, $^3J_{CP}$ = 11 Hz, meta-C), 131.2 (dd, $^1J_{CH}$ = 161 Hz, $^4J_{CP}$ = 2.5 Hz, para-C); IR (KBr) ν (cm^{-1}) 945 (C–P); MS, *m/e* 572 (M^+), 495 (M^+ – Ph). Anal. Calcd for $C_{35}H_{31}PZr$ (573.85): C, 73.26; H, 5.45. Found: C, 73.06; H, 5.08.

(8) Below –102 °C the Cp ^{1}H NMR resonance splits into a doublet ($\Delta\nu$ = 41 Hz at –114 °C, 80 MHz).

(9) X-ray diffraction data for $C_{35}H_{31}ZrP$, **1c**: crystal size (mm), 0.07 × 0.58 × 0.36; orthorhombic, space group *Pbca*; a = 10.927 (1) Å, b = 17.998 (3) Å, c = 28.992 (2) Å, Z = 8; V = 5701.4 Å^3, d_{calcd} = 1.34 g/cm^{-3}, μ(Mo Kα) = 4.54 cm^{-1} (empirical absorption correction); F(000) = 2368; data were collected on an Enraf-Nonius CAD-4 diffractometer; radiation Mo Kα (graphite monochromated), λ = 0.710 69 Å; scan mode θ–2θ; T = 21 °C; measured reflections ($+h,+k,+l$), 1.1° < θ < 28.4°, 7918; redundant data averaged to 7156 reflections; unique observed refections 3442 ($I > 2\sigma(I)$); structure solved by heavy-atom method; hydrogen atom positions were located (except at Cp10 and Ph14 and kept fixed in the final refinement stages (least squares, three blocks); number of variables, 334; R = 0.044; R_w = 0.050; $w = 1/\sigma^2(F_o)$; EOF = 2.15; residual electron density, 0.30 e Å^{-3}.

(10) (a) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (b) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. Erker, G.; Kropp, K. *Organometallics* **1982**, *1*, 1246. Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C., submitted for publication in *Angew. Chem.* (c) Dvorak, J.; O'Brien, R. J.; Santo, W. *J. Chem. Soc., Chem. Commun.* **1970**, 411. Boekel, C. P.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1974**, *81*, 371. Boekel, C. P.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1975**, *102*, 161.

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from the reaction of **5a** with methylenetriphenylphosphorane (Scheme II).[12]

Our findings indicate that this new reaction type leading to **1c** is fundamentally different from the previously reported base-induced formation of **1a**.[4] The intramolecular H transfer in the postulated (η^2-aryne)($CH_2{=}PPh_3$)$ZrCp_2$ intermediate can formally be described as a homo-1,3-hydrogen migration: an organometallic analogue of a thermally induced methylcyclopropane to 1-butene rearrangement. The question whether the organometallic hydrogen shift proceeds by a similar stepwise mechanism[13] is the subject of further studies.

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Registry No. **1c**, 96482-76-7; **2d**, 96482-77-8; **1e**, 96482-78-9; **2**, 3487-44-3; **3**, 37342-97-5; **4**, 12636-72-5; **5**, 51177-89-0; **5a**, 63672-39-9; **7**, 1291-45-8.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, atomic coordinates, interatomic distances, and bond angles (48 pages). Ordering information is given on any current masthead page.

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[12] A mixture of **1d** and **1e** was obtained analogously to **1c** (71.2% isolated yield). Anal. Calcd for $C_{36}H_{33}PZr$ (587.85): C, 73.56; H, 5.66. Found: C, 73.04; H, 5.94. **1e** (para isomer): ^1H NMR (CD_2Cl_2) δ 5.85 (s, 10 H, Cp), 5.55 (d, $^2J_{HP}$ = 13.6 Hz, 1 H, C*H*=P), 1.24 (s, 3 H, CH_3), 6.67–8.09 (m, 19 H, Tol, PPh_3); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 15.9; ^{13}C NMR (CD_2Cl_2) δ 108.3 (d, $^1J_{CH}$ = 172 Hz, Cp); 105.4 (dd, $^1J_{CH}$ = 116 Hz, $^1J_{CP}$ = 28 Hz, ylide-C), 176.9 (s, C1), 142.8 (d, $^1J_{CH}$ = 154 Hz, C2), 126.6 (d, $^1J_{CH}$ = 152 Hz, C3), 132.1 (s, C4), 21.2 (q, $^1J_{CH}$ = 126 Hz, CH_3), 128–135 (-PPh_3). **1d** (meta isomer): ^1H NMR (CD_2Cl_2) δ 5.85 (s, 10 H, Cp), 5.57 (d, $^2J_{HP}$ = 13.6 Hz, 1 H, C*H*=P), 1.17 (s, 3 H, CH_3), 6.67–8.09 (m, 19 H, Tol, PPh_3) $^{31}P\{^1H\}$ NMR (C_6D_6) δ 15.8; ^{13}C NMR (CD_2Cl_2) (atom numbering according to Figure 1) δ 108.2 (d, $^1J_{CH}$ = 172 Hz, Cp), 105.7 (dd, $^1J_{CH}$ = 116 Hz, $^1J_{CP}$ = 28 Hz, ylide-C), 181.5 (s, C1), 143.8 (d, $^1J_{CH}$ = 152 Hz, C2), 134.2 (s, C3), 123.9 (d, $^1J_{CH}$ = 154 Hz,C4), 125.3 (d, $^1J_{CH}$ = 154 Hz, C5), 139.7 (d, $^1J_{CH}$ = 154 Hz, C6), 21.8 (q, $^1J_{CH}$ = 125 Hz, CH_3), PPh_3: 134.7 (d, $^1J_{CP}$ = 80 Hz), 133.4 (dd, $^1J_{CH}$ = 162 Hz, $^1J_{CP}$ = 9 Hz, ortho-C), 128.7 (dd, $^1J_{CH}$ = 163 Hz, $^3J_{CP}$ = 11 Hz, meta-C), 131.2 (dd, $^1J_{CH}$ = 162 Hz, $^4J_{CP}$ = 2.5 Hz, para-C).

[13] Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981: pp 35–39.

A Skewed Bridging Alkyne Adduct of a d^3–d^3 Tungsten Dimer: $W_2(\mu\text{-}NMe_2)_2(\mu\text{-}C_2Me_2)Cl_4(py)_2$

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Summary: Addition of MeC≡CMe (1 equiv) to a hydrocarbon solution of $W_2Cl_2(NMe_2)_4$ gives, in the presence of pyridine, $W_2Cl_2(NMe_2)_4(py)_2(\mu\text{-}C_2Me_2)\cdot py$, I, which is unstable with respect to ligand redistribution yielding $W_2Cl_4(NMe_2)_2(py)_2(\mu\text{-}C_2Me_2)$, II, and $W_2(NMe_2)_6$. Molecules of II have a virtual C_2 axis of symmetry and a W_2C_2 unit which appears intermediate between a dimetallatetrahedrane (a perpendicular alkyne adduct) and a 1,2-dimetallacyclobutadiene (a parallel alkyne adduct).

Bridging alkyne adducts of dinuclear transition-metal complexes fall into two general types, namely, those containing perpendicular (θ = 90°) or parallel (θ = 0°) bonded alkynes where the nomenclature is derived from the angle, θ, between the μ-C–C and M–M bond vectors.[1] Hoffman, Hoffmann, and Fisel[1] have elaborated upon the reasons for this general occurrence and noted that the preference for one structure over the other has in most instances an understandable electronic origin. Though deviations from the idealized perpendicular and parallel modes of bonding have been observed, the twisting has always been relatively small. Only in dinuclear compounds containing *two* bridging alkynes have the μ-C–C bond vectors been notably twisted, e.g., twisted from the idealized perpendicular geometry by an average of 11° in $Cp_2Nb_2(CO)_2(C_2Ph_2)_2$[2] and 20° in $(t\text{-}BuO)_4W_2(\mu\text{-}C_2Ph_2)_2$.[3] However, these compounds are not in the same class as 1:1 alkyne adducts and their limiting structures cannot conform to either dimetallatetrahedranes or 1,2-dimetallacyclobutadienes. We describe here our discovery of a compound where θ = 55° which is approaching the idealized intermediate geometry for the interconversion of a perpendicular acetylene (a dimetallatetrahedrane) with a parallel acetylene complex (a 1,2-dimetallacyclobutadiene). This finding contrasts with over a dozen structurally characterized alkyne adducts of d^3–d^3 tungsten dimers: $W_2(OR)_6(py)_n(\mu\text{-}C_2R_2')$[4-6] (R = *t*-Bu, *n* = 1, R′ = H; R = *i*-Pr, *n* = 2, R′ = H; R = CH_2-*t*-Bu, *n* = 2, R′ = H; R = CH_2-*t*-Bu, *n* = 1, R′ = Me, Et and Ph) and $W_2Cl_n(NMe_2)_{6-n}L_2(\mu\text{-}RCCR')$[7,8] (L = PMe_3, PMe_2Ph, or py; R = R′ = H, Me; R = H, R′ = Ph), all of which adopt the perpendicular bonding mode.

Addition of MeC≡CMe (1 equiv) to a toluene solution of $W_2Cl_2(NMe_2)_4$ in the presence of pyridine (>3 equiv) at room temperature produces a blue-green microcrystalline precipitate within 1.5 h. This solid is formulated as $W_2(\mu\text{-}NMe_2)_2(NMe_2)_2Cl_2(py)_2(\mu\text{-}C_2Me_2)\cdot(py)$, I, on the basis of elemental analyses and low-temperature ^1H NMR spectroscopy.[9] Compound I is not stable in aromatic hydrocarbon solvents at room temperature and is labile to ligand redistribution reactions. Compound II is isolated as an orange cyrstalline solid in ca. 70% yield based on the ligand redistribution reaction shown in eq 1.[9]

$$2W_2Cl_2(NMe_2)_4(py)_2(C_2M_2)\cdot(py) \xrightarrow[\text{toluene}]{25\ ^\circ C} \underset{\text{II}}{W_2Cl_4(NMe_2)_2(C_2Me_2)(py)_2} + W_2(NMe_2)_6 + MeCCMe + 4py \quad (1)$$

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[9] Dry and oxygen-free solvents and atmospheres were used throughout. Anal. Found (Calcd) for $W_2Cl_2(NMe_2)_4(py)_2(C_2Me_2)\cdot(py)$, I: C, 31.8 (32.3); H, 4.4 (4.5); N, 8.9 (9.8); Cl, 8.1 (7.1). For $W_2Cl_4(NMe_2)_2(py)_2(C_2Me_2)$, II: C, 26.5 (26.7); H, 3.4 (3.5); N, 6.8 (6.9); Cl, 17.3 (17.5). ^1H NMR data for $W_2Cl_2(NMe_2)_4(py)_2(C_2Me_2)\cdot py$ (−45 °C, 360 MHz, CD_2Cl_2, δ in ppm relative to Me_4Si): δ 7.10–9.25 (m, 15 H, py), 3.10 (s, 6 H, NMe), 2.96 (s, 6 H, NMe), 2.84 (s, 6 H, NMe), 2.80 (s, 6 H, NMe), 2.38 (s, 6 H, C_2Me_2). ^1H NMR data for II (+22 °C, 360 MHz, CD_2Cl_2): δ 9.23 (d, *J* = 7.5 Hz, 4 H, py), 8.03 (t, *J* = 7.04 Hz, 2 H, py), 7.62 (t, *J* = 7.3 Hz, 4 H, py), 4.23 (s, 6 H, NMe), 3.68 (s, 6 H, NMe), 2.45 (s, 6 H, C_2Me_2). $^{13}C\{^1H\}$ NMR spectral data for II (+22 °C, 75.4 MHz, CD_2Cl_2, δ in ppm relative to Me_4Si) δ 213.5 (C_2Me_2), 154.9, 140.2, 124.7 (NC_5H_5), 64.1, 57.0 ($N(CH_3)_2$), 22.2 (C_2Me_2).

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