Table I. Association Constants

receptor	guest	K_a	receptor	guest	K_a
4a	**5**	2500	**4d**	**5**	1100
4b	**5**	6700	**4e**	**5**	670
4c	**5**	2000	**4e**	**6**	340

treatment with PBr_3 in CCl_4. Condensation with 2,6-bis(acylamino)-4-pyridone **8a**[2,11] (K_2CO_3, DMF) gave **9** (Scheme IV). Binding to **5** gave a 2:1 complex,[12] while the thymine photodimer **10**[13] gave a 1:1 complex (K_a = 4800 M^{-1}). Model studies for the photolyase system[14] and template synthesis of thymine derivatives are currently underway.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research.

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(12) The statistically corrected association constants for 9 with **5** were K_1 = 1250 and K_2 = 400; for **8b** with **5**, K_a = 960.

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An η^4-Benzene Species Mediates Acetylene Cyclotrimerization

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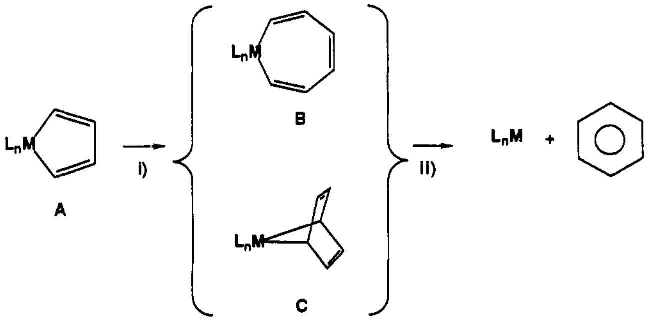
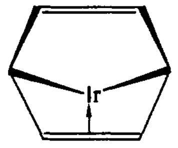
Received February 7, 1991

The mechanism of alkyne cyclotrimerization is widely discussed,[1-9] but most[10] experiments do not strongly distinguish between the generally considered two paths (via B and C) from metallacyclopentadiene (A) to free arene. We now report results wherein systematic variation of M from Rh to Ir, with L_n = $MeC(CH_2PPh_2)_3$ (triphos), appears to eliminate intermediate B, yet C is a still an imperfect representation of the mechanism.



We reported earlier[11] that a species isolated and spectroscopically characterized as the complex (triphos)RhCl(η^2-C_4H_4) (Figure 1a)[12] is catalytically active for acetylene cyclotrimerization (6 turnovers/h at 1 atm of C_2H_2 and 25 °C). No additional intermediates were detected and, in particular, no experimental evidence was provided for distinguishing between paths B and C. However, when HCCH is passed through a THF solution of (triphos)IrCl(C_2H_4) at 25 °C in the presence of a chloride scavenger[13] ($TlPF_6$), solution ^1H and $^{31}P\{^1H\}$ NMR data show the production of (triphos)Ir$(C_6H_6)^+$, which can be isolated as its BPh_4^- salt. The structure[14] of this cation (Figure 1b) shows it to be an 18-electron species with η^4 coordination of the C_6H_6 ligand. The dihedral angle within the bent benzene is 134.8°. The nonbonded carbons, C50 and C51, have Ir/C distances longer than 2.97 Å, and they are connected by a localized double bond of length 1.36 (3) Å. The observed C–C bond lengths share with all previous η^4-benzene structures[15] the C/C bond length pattern shown in D. This is symptomatic of a large degree of backbonding,[16,17] which is appropriate for a 5d metal ligated by three electron-donating ligands (triphos).[18]



D

The variable-temperature $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ show (triphos)Ir$(\eta^4$-$C_6H_6)^+$ to be fluxional. The rapid-exchange spectrum (>313 K) shows a single line, which transforms at low temperature to an AM_2 pattern. Simulation (DNMR3) yields (253–313 K) $\Delta H^* = 10.9 \pm 0.3$ kcal/mol and $\Delta S^* = -25 \pm 1$ cal K^{-1} mol^{-1}. Variable-temperature ^1H NMR spectra in $CDCl_3$ show one broad resonance (5.18 ppm) for the C_6H_6 ring at 323

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(12) Crystal data for $C_{45}H_{43}ClP_3Rh\cdot CH_2Cl_2\cdot 0.5C_7H_{16}$ (−155 °C): a = 10.133 (1) Å, b = 23.620 (4) Å, c = 18.682 (3) Å, β = 93.62 (0)° with Z = 4 in space group $P2_1/c$. $R(F)$ = 0.063 and $R_w(F)$ = 0.061 for 2038 reflections with $F > 3\sigma(F)$ and anisotropic thermal parameters on Rh, Cl, and P.

(13) $TlPF_6$ is not required for cyclotrimerization by the more labile rhodium analogue.

(14) Crystal data for $C_{71}H_{65}BrIrP_3\cdot C_5H_{10}O$ (−155 °C): a = 16.471 (6) Å, b = 17.126 (6) Å, c = 12.030 (4) Å, α = 101.22 (2)°, β = 93.61 (2)°, γ = 75.46 (1)°, with Z = 2 in space group $P\bar{1}$. $R(F)$ = 0.0845 and $R_w(F)$ = 0.0819 for 7211 absorption-corrected reflections with $F > 3\sigma(F)$ and anisotropic thermal parameters.

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(18) This pattern of C/C bond lengths is *not* seen in (triphos)M(butadiene)$^+$ species of group VIII metals and thus is specific to the η^4-benzene ligand in an electron-rich environment.

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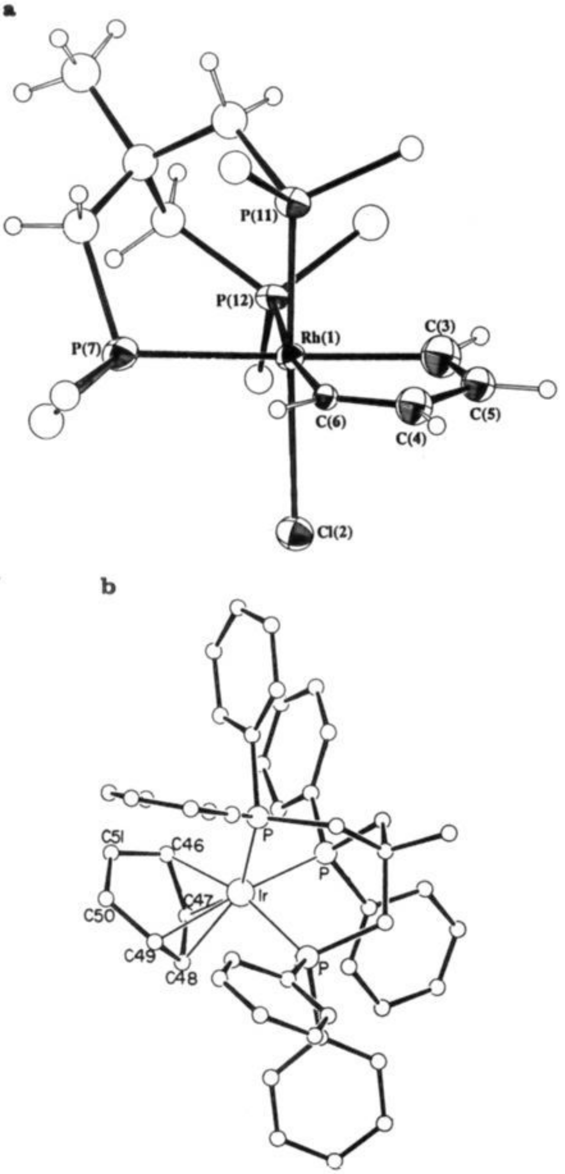
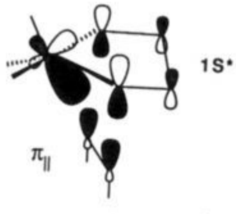


Figure 1. (a) ORTEP drawing of (triphos)Rh(C_4H_4)Cl, showing only the phenyl ipso carbons. Selected bond lengths (Å): Rh1–C3 = 2.119 (20), Rh1–C6 = 2.049 (17), C3–C5 = 1.305 (25), C5–C4 = 1.448 (25), C4–C6 = 1.283 (23). (b) ORTEP drawing of the non-hydrogen atoms of (triphos)Ir(C_6H_6)$^+$. Selected bond lengths (Å): Ir–P = 2.313 (4)–2.327 (4), Ir–C46 = 2.23 (2), Ir–C47 = 2.25 (2), Ir–C48 = 2.18 (2), Ir–C49 = 2.20 (2), C46–C47 = 1.49 (3), C47–C48 = 1.37 (3), C48–C49 = 1.49 (3), C49–C50 = 1.42 (3), C51–C46 = 1.37 (3). ∠P–Ir–P = 88.04 (13)–88.55 (13)°.

K, which transforms at lower temperatures to three equally intense lines, at 6.49, 5.86, and 3.16 ppm. These ^{1}H NMR line shapes (233–303 K) can all be simulated satisfactorily by using the same rate constants which pertain to the phosphorus site exchange. A single rate process is thus sufficient to accomplish the dynamic NMR behavior of both ^{1}H and ^{31}P nuclei, and a single mechanism is implied. Moreover, since the *rate* of phosphorus site exchange in (triphos)Ir(η^4-L)$^+$ (L = C_6H_6 or C_4H_6) is considerably higher for the η^4-benzene than for the butadiene example,[19] coordination to iridium of the pendant benzene C=C bond is implicated in that fluxional process; either an (η^3-triphos)Ir(η^6-C_6H_6)$^+$[20] intermediate or (η^2-triphos)Ir(η^6-C_6H_6)$^+$ can explain all of the observations. The very negative $\Delta S^\ddagger$ is consistent[21,22] with the fact that this fluxional motion is unrelated to the benzene *liberation* step of the catalytic reaction, which should have $\Delta S^\ddagger > 0$. In fact (see below), benzene loss does not occur at 25 °C, and when it does occur, it is triggered by substrate (acetylene).

To better understand step i, the orbitals of the presumed intermediate $P_3MC_4H_4^+$ (**1**, P = PH_3) in an square-pyramidal structure[23] were determined by means of EHT calculations. The



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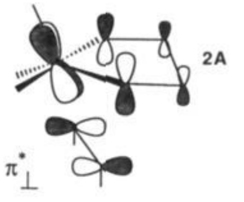

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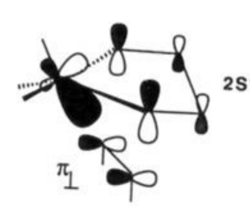

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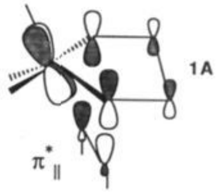

5

frontier orbitals of **1** (1A and 2A occupied; 1S* and 2S* empty) which play a role in the addition of acetylene have a strong component on the metal (3a′ and 1a″) and the π orbitals (Ψ_2 and Ψ_3) of the butadiene skeleton.[24] The low-lying LUMO (1S* shown in **2**) of the complex comprises primarily the in-phase combination of the empty metal 3a′ orbital with Ψ_3. This orbital is largely localized on the metal and is directed to overlap with $\pi_\parallel$ of the incoming acetylene. It functions mainly to form the Ir/alkyne bond although some additional C_α/alkyne bond formation is also achieved. Only slightly higher in energy one finds the antibonding combination of the same two orbitals (2S* shown in **3**). This orbital is perfectly adapted to interact with $\pi_\perp$ and allows concerted formation of the Ir/alkyne and C_α/alkyne bonds. Among the occupied orbitals of **1**, one of the highest orbitals is the antibonding combination of 1a″ and Ψ_2, 2A, shown in **4**. It is suited for interacting with $\pi^*_\perp$ and thus for concerted formation if Ir/alkyne and C_α/alkyne bonds. Somewhat lower one finds the in-phase combination of 1a″ and Ψ_2 (1A, shown in **5**), which is well adapted to interact with $\pi^*_\parallel$ and thus form both Ir/alkyne and C_α/alkyne bonds. It is clear that P_3Ir(η^2-C_4H_4)$^+$ has the required characteristics for interacting with all four π orbitals of the incoming alkyne and therefore for providing a concerted path to the η^4-benzene species, and not the metallanorbornadiene species **C**.

Treatment of (triphos)Ir(η^4-C_6H_6)$^+$ with ethyne in THF at 60 °C shows (GC) production of benzene at a rate of 0.5 mol of benzene (mol of catalyst)$^{-1}$ h^{-1}, over a 3-h period. ^{31}P{^{1}H} NMR showed the η^4-benzene compound to be the only detectable species both during and after a catalytic run.

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Acknowledgment. C.B. thanks the EEC for contract SC1.0027.C. The Laboratoire de Chimie Théorique is associated with the CNRS (URA 506) and is a member of ICMO and IPCM. C.C. thanks the CNRS for a BDI fellowship. This work was supported by an NSF/CNRS grant for international U. S./France scientific collaboration (K.G.C. and O.E.).

Supplementary Material Available: Positional and thermal parameters for (triphos)RhCl(C_4H_4) and [(triphos)Ir(C_6H_6)]-BPh_4·THF (6 pages). Ordering information is given on any current masthead page.

Nucleobase Complexes with Metal–Metal Dative Bonds: Mixed Pt,Pd Compounds with Bridging 1-Methylcytosinato Ligands and Unprecedented Short Pt(II)–Pd(II) Contacts

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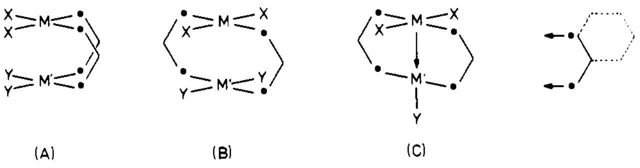
Received March 28, 1991

Metal–metal dative bond formation in complexes containing d^8 metal ions is relatively rare in organometallic and coordination chemistry[2] considering the large number of examples with weaker metal–metal "interactions" via the d_{z^2} orbital(s) of the d^8 metal(s). We report here on the facile formation of three mixed Pt,Pd complexes containing two bridging anionic 1-methylcytosine (1-MeC^-) nucleobases and on their structures which display unprecedented short Pt–Pd distances.

Dinuclear complexes of the types *cis*-$[X_2M(L)_2M'Y_2]^{n+}$, containing the d^8 metal ions M = M′ = Pt(II) or Pd(II), or M = Pt(II) and M′ = Pd(II), and two 1,2-difunctional ligands L,[3–6] as well as additional X and Y ligands (typically NH_3, amines, or halogens), virtually always are built up such that the metal coordination planes face each other (A in Chart I). Intracomplex M–M′ distances are usually around 2.8–3 Å. In the case of M = M′ = Pt(II), oxidation of the two metals is facilitated, either to mixed-valence-state compounds[7] or to diplatinum(III) species.[8]

Chart I



From model building it is obvious that a similar arrangement is impossible for the corresponding trans complexes due to severe steric hindrance between X and Y ligands (B). Only with nonheterocyclic bridging ligands having a larger bite distance are compounds of type B formed.[9]

As has recently been shown by us,[10] *trans*-$[(NH_3)_2Pd(1\text{-}MeC\text{-}N3)_2]^{2+}$,[11] when reacted with *trans*-$[(NH_3)_2Pd(H_2O)_2]^{2+}$, escapes the steric clash between X = Y = NH_3 ligands in a hypothetical *trans*-$[(NH_3)_2Pd(1\text{-}MeC^-\text{-}N3,N4)_2Pd(NH_3)_2]^{2+}$ by isomerization to the corresponding cis complex (head–tail). We have now observed another pattern by which steric hindrance between X and Y ligands is prevented, yet the trans geometry of both metals is maintained: When *trans*-$[(NH_3)_2Pt(1\text{-}MeC\text{-}N3)_2](NO_3)_2$ (**1**)[12] is reacted with *trans*-$[(NH_3)_2Pd(H_2O)_2]^{2+}$[13] in H_2O,[14] *trans*-$[(NH_3)_2Pt(1\text{-}MeC^-\text{-}N3,N4)_2Pd(NH_3)](NO_3)_2 \cdot 3H_2O$ (**2**) is formed in high yield. The structure[15] of **2** (C in Chart I and Figure 1) reveals an essentially square-planar coordination geometry of Pd and a square-pyramidal one for Pt with Pd in the apical position. Pd and Pt coordination planes are virtually at right angles (88.4 (2)°). The two metals are bridged by two almost parallel (dihedral angle 9.1 (1)°) 1-methylcytosinato anions, trans with respect to Pt, in a head–head arrangement. Pd is surrounded by two deprotonated amino groups of 1-MeC^-, an NH_3, and a Pt. The second NH_3, which originally was bound to Pd, has been lost during the reaction. The metal–metal distance

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(1) (a) Universität Dortmund. (b) Università di Trieste.

(2) See, e.g.: (a) Frew, A. A.; Muir-Manojlovic, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1980**, 624. (b) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Muir-Manojlovic, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500. (c) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014. (d) Arsenault, G. J.; Anderson, C. M.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 2094. (e) McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564. (f) Uson, R.; Forniés, J.; Tomás, M.; Casas, J. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 748. (g) Balch, A. L.; Rowley, S. P. *J. Am. Chem. Soc.* **1990**, *112*, 6139.

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(5) For Pt,Pd, see, e.g.: Micklitz, W.; Riede, J.; Huber, B.; Müller, G.; Lippert, B. *Inorg. Chem.* **1988**, *27*, 1979.

(6) References 3–5 do not include examples with two nonheterocyclic bridging ligands.

(7) See, e.g.: (a) Barton, J. K.; Rabinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827. (b) Matsumoto, K.; Fuwa, K. *J. Am. Chem. Soc.* **1982**, *104*, 897. (c) Renn, O.; Albinati, A.; Lippert, B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 84.

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(11) Abbreviations used: 1-MeC-*N3* = neutral 1-methylcytosine, $C_5H_7N_3O$, with metal at N3; 1-MeC^--*N3*,*N4* = 1-methylcytosinate anion with metals binding via N3 and the deprotonated amine group; 1-MeU = 1-methyluracilate anion, $C_5H_5N_2O_2$.

(12) Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *Inorg. Chem.* **1981**, *20*, 808.

(13) Prepared in situ from *trans*-$(NH_3)_2PdCl_2$ and $2Ag^+$ in H_2O.

(14) Preparation of **2**: *trans*-$[(NH_3)_2Pd(H_2O)_2]X_2$ (X = NO_3^- or ClO_4^-) and **1** were mixed in a 1:1 ratio in H_2O, the pH was adjusted to 8, and the sample was kept for 18 h at 22 °C. On slow evaporation at 4 °C, mixtures of **1** and **2** were obtained initially. Red plates of pure **2** were isolated only toward the end of the crystallization procedure, in ca. 5% yield, although ^1H NMR spectroscopy clearly indicates a yield of at least 60% under the conditions of the experiment. Satisfactory elemental analysis (C, H, N) was obtained for the ClO_4 salt trihydrate, NO_3 salt directly used for the X-ray analysis.

(15) Crystallography: (**2**) $C_{10}H_{21}N_{11}O_8PdPt \cdot 3H_2O$, space group $P\bar{1}$, a = 7.207 (2) Å, b = 11.692 (3) Å, c = 15.457 (4) Å, α = 108.89 (1)°, β = 101.13 (1)°, γ = 92.79 (1)°, V = 1200.4 (5) Å^3, D_{calcd} = 2.15 g cm^{-3}, D_{measd} = 2.16 g cm^{-3}, Z = 2, R = 0.037, R_w = 0.043, for 4379 unique reflections. (**3**) $C_{10}H_{18}N_9O_5PdPtCl \cdot H_2O$, space group $P\bar{1}$, a = 9.116 (4) Å, b = 10.508 (6) Å, c = 11.370 (6) Å, α = 115.33 (2)°, β = 90.00 (3)°, γ = 92.62 (3)°, V = 983.1 (9) Å^3, D_{calcd} = 2.36 g cm^{-3}, D_{measd} = 2.32 g cm^{-3}, Z = 2, R = 0.038, R_w = 0.048, for 4960 unique reflections. (**4**) $C_{15}H_{23}N_{11}O_7PdPt \cdot 3H_2O$, space group $P\bar{1}$, a = 9.956 (5) Å, b = 10.619 (6) Å, c = 14.460 (4) Å, α = 68.66 (4)°, β = 85.88 (3)°, γ = 67.10 (4)°, V = 1307 (1) Å^3, D_{calcd} = 2.09 g cm^{-3}, D_{measd} = 2.10 g cm^{-3}, Z = 2, R = 0.39, R_w = 0.047, for 5023 unique reflections. Diffraction data were collected by using a CAD-4 Enraf-Nonius single-crystal diffractometer with Mo Kα radiation (λ = 0.7107 Å). All the structures were solved by conventional Patterson and Fourier methods and refined by full-matrix anisotropic least-squares methods. The contributions of the hydrogen atoms (kept at calculated positions) were included in the final refinements.

0002-7863/91/1513-5129$02.50/0