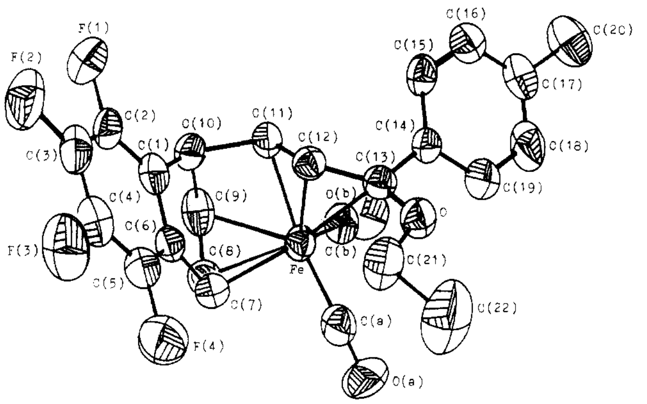
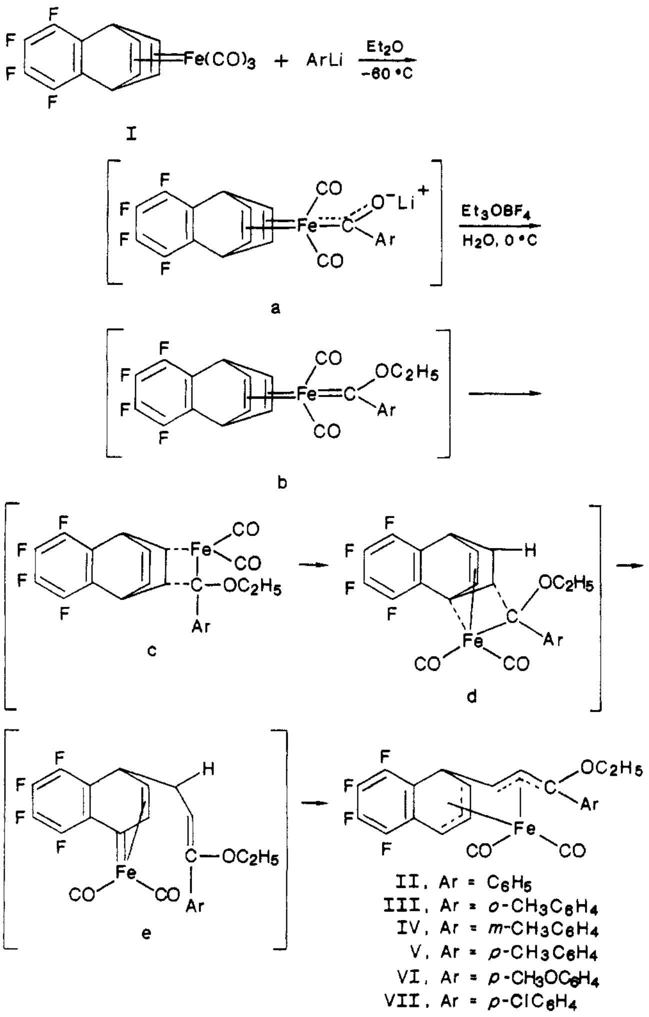


Figure 1. A drawing of $C_{24}H_{18}O_3F_3Fe$ (V) showing the molecular structure and atom numbering. Selected bond lengths (Å) and angles (deg) include the following: Fe–C(a), 1.764 (4); Fe–C(b), 1.769 (4); Fe–C(7), 2.191 (4); Fe–C(8), 2.061 (4); Fe–C(9), 2.239 (3); F–C(11), 2.110 (3); Fe–C(12), 2.063 (3); Fe–C(13), 2.253 (3); C(7)–C(8), 1.409 (6); C(8)–C(9), 1.379 (6); C(9)–C(10), 1.528 (5); C(10)–C(11), 1.526 (4); C(11)–C(12), 1.405 (4); C(12)–C(13), 1.410 (4); C(1)–C(6), 1.398 (5); C(6)–C(7), 1.464 (5); C(13)–C(14), 1.472 (5); C(13)–O, 1.388 (4); C(14)–C(13)–O, 107.8 (2); C(12)–C(13)–C(14), 126.2 (3); C(12)–C(13)–O, 120.5 (3); C(6)–C(7)–C(8), 117.1 (3); C(7)–C(8)–C(9), 116.8 (3); C(8)–C(9)–C(10), 119.8 (4); C(9)–C(10)–C(1), 112.3 (3); C(10)–C(1)–C(6), 116.4 (3); C(1)–C(6)–C(7), 119.0 (3); C(9)–C(10)–C(11), 94.6 (3); C(10)–C(11)–C(12), 122.3 (3); C(11)–C(12)–C(13), 121.8 (3).

Scheme I



elemental analyses and IR, ^{1}H NMR, and mass spectroscopic measurements. The structure of V was verified by a single-crystal X-ray structure determination.

The molecular structure of V (Figure 1)[8] shows that a six-membered ring of the tetrafluorobenzobicyclo[2.2.2]-octatriene ligand is opened with breaking of an original σ bond corresponding to C(7)–C(12) in the tetrafluorobenzobicyclo[2.2.2]octatriene moiety. The carbon atom C(12) is now bonded to the "carbene" carbon atom C(13) forming a new σ bond. In addition, two π-allyl groups composed of C(7)–C(8)–C(9) and C(11)–C(12)–C(13), respectively, are bonded side-on to the orbitals of the central iron atom to satisfy the 18-electron rule. More interestingly, the six-membered ring containing a π-allyl ligand adopts a twisted boat conformation.

Acknowledgment. We thank the Science Foundation of the Chinese Academy of Sciences and the National Science Foundation of China for financial support of this work.

Registry No. I, 12130-08-4; II, 110718-70-2; III, 110718-71-3; IV, 110718-72-4; V, 110718-73-5; VI, 110718-74-6; VII, 110718-75-7; C_6H_5Li, 591-51-5; o-$CH_3C_6H_4Li$, 6699-93-0; m-$CH_3C_6H_4Li$, 10325-82-3; p-$CH_3C_6H_4Li$, 2417-95-0; p-$CH_3OC_6H_4Li$, 14774-77-7; p-ClC_6H_4Li, 14774-78-8.

Supplementary Material Available: General procedures for the preparations of complexes II–VII and tables of crystallographic data, final fractional atomic coordinates and thermal parameters, bond lengths and angles, and least-squares plane for V (8 pages); a listing of structure factors for complex V (15 pages). Ordering information is given on any current masthead page.

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[8] $C_{24}H_{18}O_3F_4Fe$: monoclinic, C^6_{2h}—$C2/c$, a = 16.870 (4) Å, b = 13.707 (4) Å, c = 19.361 (4) Å, β = 107.92 (2)°, V = 4259 (1) Å^3, Z = 8, D_{calcd} = 1.51 g/cm^3, μ = 7.9 cm^{-1} (Mo Kα). A total of 4068 unique reflections were collected within the range of 3° ≤ 2θ ≤ 50° in the conventional $\theta/2\theta$ scan mode, of which 2481 observed reflections ($I > 3\sigma(I)$) were used in the structure solution (Patterson method and differential Fourier synthesis) and refinement (block-matrix least-squares method) to give final R = 0.0409 and R_w = 0.0391.

The Mechanism of the Wacker Process. Corroborative Evidence for Distal Addition of Water and Palladium

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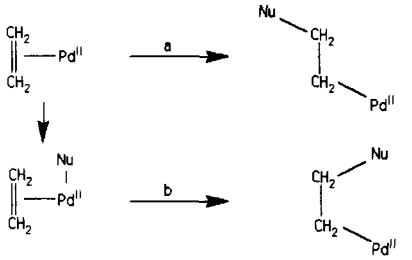
Received May 28, 1987

Summary: Water adds to 1,2-dimethyl-1,4-cyclohexadiene in the presence of bis(acetonitrile)palladium dichloride in aqueous acetone to afford predominately *trans*-bis(5-hydroxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)-palladium chloride (**2**), as well as the Wacker oxidation product 3,4-dimethyl-3-cyclohexen-1-one (**3**). The trans stereochemistry of the (η^3-allyl)palladium complex **2** confirms distal addition of water and palladium to the less substituted double bond of the cyclohexadiene.

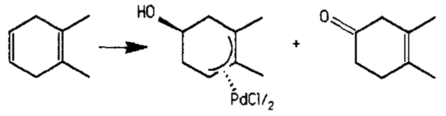
The Wacker process for oxidation of ethylene to acetaldehyde is one of the first examples of the successful industrial application of homogeneous catalysis. As a consequence its mechanism has been extensively studied and the reaction is a classic example of transition-metal-promoted nucleophilic addition to unactivated alkenes.[1]

It is generally accepted that a σ-(β-hydroxyalkyl)palladium complex is the intermediate; however, the stereochemistry of the addition, distal (pathway a) or proximal (pathway b), apparently still remains ambiguous in some quarters.

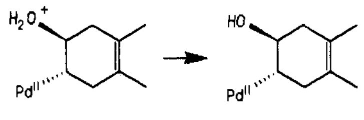


Kinetic evidence has been used to suggest that the σ-(β-hydroxyalkyl)palladium intermediate is formed by insertion of the alkene into the palladium-oxygen bond of a hydroxypalladium species (pathway b),[2] although the data are also consistent with trans stereochemistry for the addition (pathway a). In contrast, stereochemical evidence derived from the addition of a number of water-related nucleophiles such as alcohols, amines, and acetate indicates that distal addition (pathway a) is preferred, while proximal addition occurs only with such nucleophiles as hydride and nonstabilized carbanions.[1b,3] This dichotomous behavior is due to the orbital energies of the nucleophiles[3,4] and has been substantiated by molecular orbital calculations.[5] Consequently, distal addition of water seems to be the more plausible mechanism (pathway a) for the Wacker oxidation and two stereochemical studies independently reached this conclusion.[6,7] However, it has been suggested that these might not be relevant to the mechanism of the Wacker process. In the first study, chloride ion and cupric chloride concentrations are higher than in the Wacker oxidation, and in the second, carbon monoxide is present. In both cases, it has been contended that the potential coordination of the chloride ion or the carbon monoxide to the palladium might have altered the reaction pathway.[8]

In connection with studies of palladium(II)-assisted nucleophilic additions to 1,4-cyclohexadienes,[9] we find that 1,2-dimethyl-1,4-cyclohexadiene and bis(acetonitrile)palladium dichoride in aqueous acetone at 20 °C in the presence of sodium bicarbonate and cupric chloride[10] affords predominately the *trans*-(η^3-allyl)palladium complex **2** (77%), as well as the Wacker oxidation product 3,4-dimethyl-3-cyclohexen-1-one (**3**, 18%).[11] Both products are presumably derived from the same palladium intermediates **1a,b**, generated by distal addition of water and palladium to the less substituted double bond of the cyclohexadiene. β-Elimination of hydride from the allylic carbon of **1b**, followed by readdition of palladium hydride from the same face,[12] produces the *trans*-(η^3-allyl)palladium complex **2**. Competing β-elimination of hydride from the carbinol carbon of **1b**, followed by readdition of palladium hydride and subsequent β-elimination of hydride from the carbinol oxygen, yields the normal Wacker product, which in this case is the cyclohexenone **3**.[13]



2 3



1a 1b

Results of this present study also perhaps suggest the actual nature of the nucleophile in the Wacker process. In the absence of bicarbonate, water still adds to 1,2-dimethyl-1,4-cyclohexadiene, albeit in lower yield. This same trend was also noted in the related palladium-initiated addition of methanol to this diene.[9a] The nucleophile in this case is probably water (and methanol in the previous study), and the function of the weak base is to deprotonate the initial water-addition intermediate **1a**, formed in a reversible process, and to drive the reaction to completion.[14]

^{1}H NMR studies clearly secure the stereochemistry assignments for **2**.[15] In addition, the structure and stereo-

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(1) (a) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic: New York, 1971; Vol. 1, pp 130–138. (b) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; Reidel: Dordrecht/Boston/Lancaster, 1980.

(2) (a) Henry, P. M. *J. Am. Chem. Soc.* **1964**, *86*, 3246–3250. (b) *Ibid.* **1966**, *88*, 1595–1597. (c) *Ibid.* **1972**, *94*, 4437–4440. (d) Moiseev, I. I.; Levanda, O. G.; Vargaftik, M. N. *Ibid.* **1974**, *96*, 1003–1007.

(3) (a) Åkermark, B.; Bäckvall, J.-E.; Zetterberg, K. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 577–585. (b) Bäckvall, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335–342.

(4) Åkermark, B.; Almemark, M.; Jutland, A. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 451–457.

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(6) (a) Bäckvall, J.-E.; Åkermark, B.; Ljunggren, S. O. *J. Chem. Soc., Chem. Commun.* **1977**, 264–265. (b) *J. Am. Chem. Soc.* **1979**, *101*, 2411–2415.

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(8) (a) Reference 1b, p 80. (b) Reference 1b, pp 71–72.

(9) (a) Hall, S. S.; Åkermark, B. *Organometallics* **1984**, *3*, 1745–1748. (b) Söderberg, B. C.; Åkermark, B.; Hall, S. S. Presented at 194th National Meeting of the American Chemical Society, New Orleans, LA, Aug 1987; paper ORGN 213.

(10) Apparently (η^3-cyclohexenyl)palladium complexes decompose in the presence of Pd(0) and cupric chloride (ca. 10–20%) is useful to reoxidize Pd(O) back to Pd(II) to minimize this reaction. However, with more cupric chloride, such as equimolar amounts, the isolated yield of complex drops again.

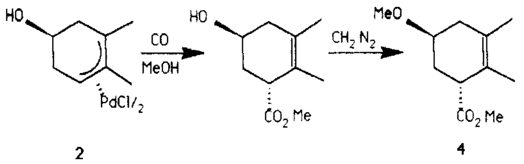
(11) To a stirred yellow slurry of 1.30 g (5.0 mmol) of bis(acetonitrile)palladium dichloride, 480 mg (4.8 mmol) of $KHCO_3$, and 136 mg (0.80 mmol) of $CuCl_2$ in 30 mL of acetone was added a suspension of 445 mg (4.00 mmol) of 1,2-dimethyl-1,4-cyclohexadiene in 3.6 mL of water and 10 mL of acetone. A dark orange solution formed immediately, and after 25 h the dark yellow slurry was filtered through a 5-mm pad of Celite (dry packed) and the filter rinsed with 150 mL of EtOAc. Concentration of the yellow filtrate (water aspirator pressure) revealed 1.05 g of a yellow oil–solid. Flash chromatography (3.5 × 23 cm SiO_2 column packed and eluted with 95:5 of EtOAc-ethanol) afforded 90 mg (18%) of 3,4-dimethyl-3-cyclohexen-1-one (**3**), followed by 817 mg (77%) of *trans*-bis(5-hydroxy-1,2-dimethyl-1-3-η^3-cyclohexenyl)palladium chloride (**2**) as a yellow oil, which slowly crystallized. Although substantial amounts of the products had already formed after only 15 min, the reaction was continued for 25 h to maximize the yield. Since the ca. 4:1 product ratio of **2** and **3** did not change with time, we conclude that they are kinetic products.

(12) (a) Parra-Hake, M.; Rettig, M. F.; Wing, R. M. *Organometallics* **1983**, *2*, 1013–1017. (b) Albelo, G.; Wiger, G.; Rettig, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 4510–4518. (c) Larock, R. C.; Mitchell, M. A. *Ibid.* **1978**, *100*, 180–188. (d) Larock, R. C.; Takagi, K.; Hershberger, S. S.; Mitchell, M. A. *Tetrahedron Lett.* **1981**, *5231*–5234.

(13) In support of this mechanism, when this experiment was performed in D_2O/acetone, no deuterium was incorporated into products **2** and **3**.

(14) This is reminiscent of the palladium-assisted amination of olefins, where the corresponding deprotonation step can be experimentally observed by using NMR techniques.[20] In both the water and methanol studies, lower yields (or no products) were also observed with stronger bases (hydroxide and methoxide). In the methanol study,[9a] none of the (η^3-allyl)palladium complex was obtained when methoxide was present, and in this study, the yields of products **2** and **3** were lower when NaOH was used. Apparently inactive hydroxy- and methoxypalladium(II) species are formed with the stronger bases.

chemistry[16] of the *trans*-(η^3-allyl)palladium complex **2** was confirmed by its transformation to methyl *trans*-5-methoxy-2,3-dimethyl-2-cyclohexene-1-carboxylate (**4**),[17] which was previously obtained by palladium(II)-assisted addition of methanol to 1,2-dimethyl-1,4-cyclohexadiene,[9a] followed by methoxycarbonylation.[9b] Insertion of carbon monoxide into palladium-carbon bonds is known to proceed with complete retention of configuration.[18]



These results[19] corroborate the previous stereochemical studies from Stille's[7] and this laboratory[6] that have provided evidence that distal addition of water and palladium to alkenes, followed by β-elimination of hydride, is the probable mechanism for the Wacker process.

Acknowledgment. We are grateful to the Swedish Board for Technical Development and the Swedish Natural Science Research Council for supporting this research.

Registry No. 2, 111059-90-6; **3**, 33475-09-1; **4**, 111026-08-5; **5**, 111026-09-6; 1,2-dimethyl-1,4-cyclohexadiene, 17351-28-9; dimethyl malonate anion, 33673-07-3; bis(acetonitrile)palladium chloride, 14592-56-4.

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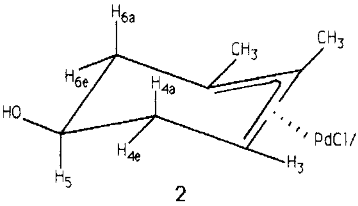
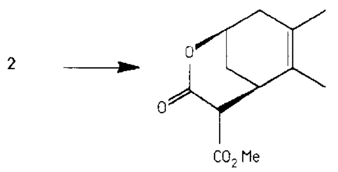
(15) Complex **2**: mp 67–70 °C; IR (KBr) 3390 (br), 2970, 2890, 2820, 1430, 1125, 1040, 995, 925, 780, 730 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.78 (1 H, H-5, apparent quintet, J = ca. 7 Hz), 4.52 (1 H, H-3, t, $J_{3,4a} = J_{3,4e} = 3.3$ Hz), 3.24 (1 H, OH, br s, exchangeable with D_2O), 2.43 (1 H, H-6e, dd, $J_{6e,6a} = 15.9$ Hz, $J_{6e,5} = 5.7$ Hz), 2.29 (1 H, H-4e, ddd, $J_{4e,4a} = 15.7$ Hz, $J_{4e,5} = 5.7$ Hz, $J_{4e,3} = 3.7$ Hz), 2.07 (3 H, MeC-2, s), 1.39 (3 H, MeC-1, s) superimposed on 1.34 (1 H, H-6a, dd, $J_{6a,6e} = 15.7$ Hz, $J_{6a,5} = 8.1$ Hz) and 1.24 (1 H, H-4a, ddd, $J_{4a,4e} = 15.1$ Hz, $J_{4a,5} = 7.8$ Hz, $J_{4a,3} = 3.0$ Hz); homonuclear decoupling, irradiation at δ 4.78 collapsed the signals at δ 2.43 and 1.34 to d and at δ 2.29 and 1.24 to dd, irradiation at δ 4.52 collapsed the signals at δ 2.29 and 1.24 to dd, irradiation at ca. δ 2.43 affected the signals at δ 4.78 and 1.34; irradiation at ca. δ 2.29 affected the signals at δ 4.78 and 1.24 and collapsed the signal at δ 4.52 to a d, irradiation at δ 1.30 affected the signals at δ 4.78, 2.43, and 2.29 and collapsed the signal at δ 4.52 to a d; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and off-resonance proton decoupling) 113.19 (s), 87.91 (s), 72.26 (d), 65.21 (d), 44.33 (dd), 37.39 (dd), 22.04 (q), 19.08 (q) ppm. Our



2

earlier work on methoxylation[9] has shown that for chair conformations in the (η^3-cyclohexenyl)palladium complexes, the vicinal axial–axial couplings are 7–9 Hz, axial–equatorial couplings are ca. 6 Hz, and the equatorial–equatorial couplings are ca. 2 Hz. The larger (ca. 8 Hz) coupling (axial–axial) between the H-5 proton and the axial protons at C-4 and C-6 and the smaller (5.7 Hz) coupling (axial–equatorial) between the H-5 proton and the equatorial C-4 and C-6 protons establish the conformation of the ring.

(16) The relative stereochemistry of the palladium complex **2** was also corroborated by its conversion to the lactone **5** with the anion of dimethyl



5

malonate. These alkylations are known to occur directly at carbon on the face of the π-allyl unit opposite the palladium. See: Trost, B. M.; Weber, L. *J. Am. Chem. Soc.* **1975**, *97*, 1611–1612.

(17) Carboxylate **4**: bp 70 °C (0.08 torr); IR (film) 2970, 2910, 2820, 1727, 1435, 1375, 1360, 1225, 1140, 1090, 960, 840 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.70 (3 H, CO_2Me, s), superimposed on 3.77–3.57 (1 H, H-5, complex m), 3.36 (3 H, OMe, s), 3.16 (1 H, H-1, m, $w_{1/2} = 11$ Hz), 2.36 (1 H, H-4e, apparent dd with further fine splitting, $J_{4e,4a}$ = ca. 17 Hz, $J_{4e,5a} = 3.8$ Hz), 2.10 (1 H, H-6e, dddd, $J_{6e,6a} = 12.9$ Hz, $J_{6e,5a} = 5.1$ Hz, $J_{6e,1e} = 3.2$ Hz, $J_{6e,4e} = 1.2$ Hz), 1.96 (1 H, H-4a, dd with further fine splitting, $J_{4a,4e}$ = ca. 17 Hz, $J_{4a,5a}$ = ca. 8 Hz), 1.79 (1 H, H-6a, ddd, $J_{6a,6e} = 12.7$ Hz, $J_{6a,5a} = 9.3$ Hz, $J_{6a,1e} = 6.1$ Hz), and two overlapping Me multiplets with signals at δ 1.67, 1.66, 1.66, 1.65, 1.64 (6 H, MeC-2 and MeC-3); homonuclear decouping, irradiation at δ 3.64 collapsed the signals at δ 2.36 and 1.96 to d and at δ 2.10 and 1.79 to dd, irradiation at δ 3.16 collapsed the signals at δ 2.10 and 1.79 to dd, irradiation at δ 2.36 collapsed the signals at δ 3.77–3.57 to an apparent ddd and at δ 1.96 to a d, irradiation at δ 2.10 collapsed the signals at δ 3.77–3.57 to an apparent ddd, at δ 3.16 to a d, and at δ 1.79 to an apparent dd, irradiation at δ 1.79 collapsed the signals at δ 3.77–3.57 to an apparent ddd, at δ 3.16 to a br s, and at δ 2.10 to an apparent dd; ^{13}C NMR (50 MHz, $CDCl_3$, broad-band proton and off-resonance proton decoupling) 175.53 (s), 127.41 (s), 122.17 (s), 73.40 (d), 55.86 (q), 51.78 (q), 46.19 (d), 37.44 (t), 30.98 (q), 19.60 (q), 17.57 (q) ppm; mass spectrum, m/z (relative intensity) 198 (M^+, 2), 167 (11), 166 (100), 139 (38), 125 (19), 107 (94), 106 (19), 91 (45), 79 (23), 58 (28), 45 (28), 41 (30). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.70; H, 9.10.

(18) Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 485–490.

(19) In contrast to 1,5-cyclooctadiene and norbornadiene (two effective bidentate ligands), 1,4-cyclohexadienes seem to behave essentially as monodentate ligands under these conditions. Only in nonpolar solvents do our NMR studies indicate some coordination by both double bonds of the 1,4-cyclohexadiene. In addition, in some 1,4-cyclohexadienes reactions where the distal addition of methanol was slow, competitive hydride addition was observed.[9b] In these cases, hydride and palladium are adding from the same face, clearly indicating that there is no hindrance to proximal attack. Consequently, substituted 1,4-cyclohexadienes are reasonably acceptable alkene models for the Wacker process.

(20) Åkermark, B.; Hegedus, L. S.; Zetterberg, K.; Olsson, L. F. *J. Am. Chem. Soc.* **1984**, *106*, 7122–7126.

Synthesis and Reactivity of Trans Isomers of Bis(phosphine)-Substituted Carbyne Complexes of Molybdenum and Tungsten: $[M(\equiv CR)X(CO)_2(PR_3)_2]$

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Summary: Irradiation with visible light of the cis bis(phosphine)-substituted molybdenum and tungsten carbyne complexes *cis,cis*-$[M(\equiv CPh)X(CO)_2(PR_3)_2]$ generates the trans isomers. The isomerization is postulated to proceed via photogenerated pentacoordinate metal ketenyl complexes. Irradiation of *cis,cis*-$[W(\equiv CPh)X(CO)_2(PMe_3)_2]$ at low temperatures in the presence of PMe_3 and PhCCH results in formation of the thermally labile tungsten ketenyl complexes $[W(\eta^2\text{-PhCCO})Cl(CO)(PMe_3)_3]$ and $[W(\eta^1\text{-PhCCO})Cl(CO)(PhCCH)(PMe_3)_2]$, respectively. Substitution of one carbonyl ligand in the trans bis(phosphine)-substituted metal carbyne complexes is demonstrated.

Bis(donor ligand)-substituted carbyne complexes of the group 6 transition metals, $[M(\equiv CR)X(CO)_2L_2]$ (M = Cr, Mo, W; X = halide; L = donor ligand),[1] which have become easily available through recently developed new synthetic methods,[2] are generally obtained as the cis L_2 derivatives.

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