In the ^{1}H NMR of **3**,[14] the metal hydrides are equivalent even at −111 °C. The metal hydride resonance for **3** in CD_2Cl_2 at −28 °C appears at δ −7.62 as a doublet of doublets (J_{PH} = 120.9 Hz, $J_{P'H}$ = −11.1 Hz) with satellites due to coupling to ^{195}Pt. The 593 Hz J_{PtH} is consistent either with an average of a terminal PtH and a noncoupled ReH or with two bridging hydrides. At higher temperature (60.7 °C), rapid exchange of the phosphine environments gives rise to a 1:2:1 triplet for the metal hydride signals. An interesting coalescence behavior of the metal hydride signals is seen. The inner lines of the doublet of doublets are due to coupling to $\alpha\alpha$ and $\beta\beta$ ^{31}P spins and remain sharp at all temperatures; the outer lines are due to coupling to $\alpha\beta$ and $\beta\alpha$ ^{31}P spins, and these lines broaden, coalesce, and sharpen to the center line of the 1:2:1 triplet as the temperature is increased. Similar temperature dependent spectra of **4** were observed by Braunstein and Geoffroy.[12] Hydride exchange while maintaining the inequivalence of the phosphine ligands requires accessing a $(\mu\text{-H})_2$ structure similar to IV which has a pseudotetrahedral d^{10} Pt center in which the phosphines remain inequivalent due to their relationship to the Cp ligand on Re. The conversion of IV back to **3** can occur via two pathways. The major pathway returns the phosphines to their original environments. The minor pathway occurs via an alternative geometry and exchanges the phosphine environments.[15]

Since access to bridging dihydride structure IV is required to explain the NMR equivalence of the metal hydrides of **3**, we considered the possibility that IV might be the solution structure of the $PtReH_2$ compound even though this seemed somewhat unlikely due to the large differences seen for J_{PH} and $J_{P'H}$. Saunders isotopic perturbation of equilibria technique[16] provides a definitive test to distinguish between symmetric $(\mu\text{-H})_2$ structure IV and nonsymmetric **3** by simply comparing the chemical shift of the $PtReH_2$ compound **3** with the PtReHD compound **3d**. If the material has terminal hydride ligands, then the equilibrium constant for HPtReD $\rightleftarrows$ DPtReH should not be unity because of differences in zero-point energy. The proton will spend more than 50% of the time on one of the metals, and the average chemical shift of **3d** will be substantially different from that of **3**. However, if the structure is $(\mu\text{-H})(\mu\text{-D})$ species IV, then a negligible difference in chemical shift would be expected. When a solution of **3** was shaken with D_2 at room temperature for 10 min, the ^{1}H NMR spectrum at 14 °C exhibited a multiplet at δ −7.62 due to **3** and a similar multiplet shifted 0.16 ppm upfield (δ −7.78) due to **3d**. When the temperature was lowered to −84 °C, the chemical shift difference increased to 0.24 ppm due to a change in the equilibrium constant. These results rule out the bridging dihydride IV as the only species in solution and are consistent with the solution structure of **3** being the same as the solid-state structure.

J_{PtH} increases from 593 Hz at 14 °C to 649 Hz at −84 °C for **3**. This variation suggests that two species are present in equilibrium. These two species have similar zero-point energies since **3d** behaves very similarly (J_{PtH} = 601 Hz at 14 °C, J_{PtH} = 654 Hz at −84 °C) and therefore cannot have different numbers of bridging and terminal hydrides. We believe this phenomenon may be due to a temperature dependent equilibrium between two rotamers of the terminal dihydride.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

Supplementary Material Available: Variable temperature ^{1}H NMR data of the hydride region of a mixture of **3** and **3d** and tables of positional and thermal parameters and interatomic distances and angles for **3** (9 pages); listing of observed and calculated structure factors (88 pages). Ordering information is given on any current masthead page.

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[13] The oxidative addition of $C_5H_5(CO)_3MoH$ to $(PPh_3)_2Pt(CH_2{=}CH_2)$ to produce **4** has been observed at du Pont. Janowicz, A. H.; Bryndza, H. E., private communication.

[14] $Cp(CO)_2(H)Re{-}Pt(H)(PPh_3)_2$ (**3**): ^{1}H NMR (270 MHz, CD_2Cl_2, 400 mm H_2, −28 °C) δ 7.3 (m, 30 H), 4.99, (s, 5 H), −7.62 (dd, J_{PH} = 120.9 $J_{P'H}$ = −11.1 Hz, 2 H, J_{PtH} = 593.4 Hz); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 400 mm H_2, 0.07 M $Cr(acac)_3$) δ 205.52 (CO), 129.96 (s, para), 139.25, (d, J_{CP} = 11.7 Hz, ortho or meta), 128.25, (d, J_{CP} = 11.7 Hz, ortho or meta), 80.98 (s, C_5H_5), ipso C not observed; ^{31}P NMR (202 MHz, CD_2Cl_2, 25 °C) δ 30.1 (t, J_{PH} = 49 Hz, J_{PtP} = 3308); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, −70 °C) δ 29.9 (J_{PtP} = 3308 Hz), 30.3 (J_{PtP} = 3308 Hz); $^{195}Pt\{^1H\}$ (107 MHz, CD_2Cl_2, 400 mm H_2, 22 °C) δ −5823.4 relative to Na_2PtCl_6 in D_2O (t, J_{PtP} = 3224 Hz); IR (KBr) 2098 (m, MH), 1906 (s, CO), 1832 (s, CO) cm^{-1}.

[15] A symmetric $(\mu\text{-H})_2$ square planar Pt(II) intermediate cannot be responsible for the equivalence of the metal hydrides since it requires equal rates for hydride and phosphine exchange. However, phosphine exchange was observed to be much slower than hydride exchange.

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Electrocatalytic Hydrogenation of Organic Compounds on Carbon Electrodes Modified by Precious Metal Microparticles in Redox Active Polymer Films

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Received May 20, 1987

In contrast to catalytic hydrogenation which is a widely used procedure in organic synthesis, electrocatalytic hydrogenation has been largely neglected despite the advantages of very mild conditions (room temperature and atmospheric pressure) normally employed in electrosynthesis. However, in recent years an increasing number of papers on this subject have appeared with the development of hydrogen active powder cathodes, particularly those based on Raney-nickel[1-3] but also Devarda-copper[2] and palladium or platinum on carbon[3] catalysts. Some electrohydrogenations with metals deposited on carbon[4] or solid polymer electrolyte membranes[5] have also been reported. On the other hand, electrodes modified by conductive,[6] redox,[7] or even electroinactive[8] polymer films in which highly dispersed platinum or palladium microparticules have been deposited show a good catalytic activity toward reduction of protons to hydrogen. We find that hydrogen liberated by electrolysis in aqueous media on carbon electrodes modified by a redox polymeric film containing

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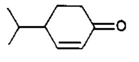
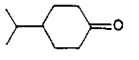
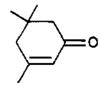
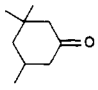
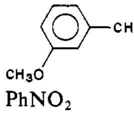
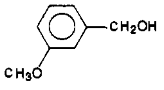
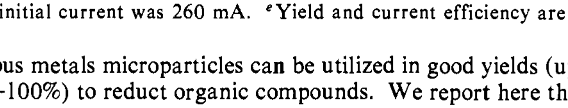
Table I. Electrochemical Hydrogenation on C/(polyV^{2+}•Pd) Electrodes[a]

entry	substrate	init amt, mmol	consmd current, electron $molecule^{-1}$	product	yield[b] (current effcncy)[e]
1	$PhCH{=}CHCO_2H$	7	2	$PhCH_2CH_2CO_2H$	95[c] (95)
2		15	2		100 (100)
3		15	9.6		48 (10)
4	$PhC{\equiv}CPh$	3	4	$PhCH_2CH_2Ph$	98 (98)
5		4	2		100 (100)
6	$PhNO_2$	8	6[d]	$PhNH_2$	86 (86)

[a] All experiments were carried out in 80 cm^3 of equimolar water/ethanol (entries 1, 3, 5, 6) or 2-ethoxyethanol (entries 2 and 4) mixtures[13] containing 0.1 M KCl; the electrolysis medium was previously deaerated (Ar), and the cell was made airtight with vacuum grease to minimize exposure to O_2. Unless otherwise noted, the electrode potential was adjusted to obtain an electrolysis current in the vicinity of 100 mA. [b] Yields were determined by HPLC (entries 1, 5, and 6) or by GC (entries 2, 3, and 4). [c] The same result was obtained with 100 and 300 mA electrolysis currents. [d] The initial current was 260 mA. [e] Yield and current efficiency are in percent.

precious metals microparticles can be utilized in good yields (up to 95–100%) to reduct organic compounds. We report here the first example of electrocatalytic hydrogenation of nitrobenzene, an aromatic aldehyde, and olefinic and acetylenic compounds on these new cathodes.

Catalytic cathodes were prepared with reagent I as the monomer[9] from which the surface-confined polymer (polyV^{2+}) can be grown by oxidative electropolymerization on carbon felt.[10] The impregnation of the (polyV^{2+}) with Pd, Pt, or Rh was effected[11] following a similar procedure described by Wrighton and coworkers.[7a–c]



I

The deposition of metal into the polymer allowed substantial H_2 evolution in aqueous media[12] for pH < 4, when the potential of the electrode was held at −0.5 V vs SCE. Current densities for H_2 evolution increased at lower pH, as expected.[7a,b] Electrolytically generated hydrogen could be directly used in the hydrogenation of organic compounds. Typically, the C/(polyV^{2+}•Pd) electrode[10,11] containing 2–5 × 10^{-5} mol of Pd was placed in the cathodic compartment of an H-shaped three-compartment electrochemical cell. The substrate was added to the catholyte,[13] and the potential of the cathode was moved from 0 to −(0.4–0.5) V vs SCE to obtain a significant electrolysis current (100–300 mA). In no case was the potential held more negatively.

Six relevant examples are presented in Table I. Carbon–carbon double and triple bonds conjugated with an aromatic ring (entries 1 and 4) or a carbonyl group (entry 2) as well as an aromatic aldehyde (entry 5) were hydrogenated with current yields close to 100%. Nitrobenzene could also be readily hydrogenated. Steric hindrance markedly decreased the efficiency, as shown by the poor yield obtained for the reduction of isophorone (entry 3). Selective hydrogenation of diphenylacetylene to stilbene was not successful, since it was always accompanied by a subsequent reduction to 1,2-diphenylethane (entry 4), even if electrolysis was stopped when two electrons per substrate molecule has been passed. Aliphatic ketones were not reduced regardless of the metal (Pd, Pt, or Rh) used, which allowed selective hydrogenation of conjugated enones (entries 2 and 3).

The stability of a C/(polyV^{2+}•Pd) electrode was tested during the hydrogenation of several cryptone samples (entry 2). The amount of 4-isopropylcyclohexanone produced far exceeded the amount of catalyst by a significant factor. Over 5000 molecules of product per Pd atom were formed, and the catalytic activity of the cathode remained apparently unchanged.

In contrast, a carbon-felt electrode on which Pd has been electrodeposited[14] showed poor stability. In these experimental conditions only 60 molecules of cryptone per Pd atom could be hydrogenated before complete loss of catalytic activity of this Cf/Pd cathode, which could be associated with significant loss or redistribution of Pd particles. This confirms the high catalytic efficiency and the excellent stability obtained with dispersed microparticles of catalyst in polymer film coated electrodes.[7,8]

In order to specify the role of the redox groups V^{2+} bounded to the polypyrrole matrix, we have also studied the behavior of a Cf/(polypyrrole•Pd) electrode.[15] This cathode appeared more stable than the Cf/Pd electrode but rather less efficient than the Cf/(polyV^{2+}•Pd) electrode. In the same experimental conditions, electrolysis currents are 2.5 times lower and the Cf/(polypyrrole•Pd) electrode has lost 75% of its catalytic activity when 120 molecules of cryptone per atom have been hydrogenated. It appears that V^{2+} groups improve markedly the conductivity and the stability of the catalytic film at −0.5V.

We have also turned to the use of other precious metals. Hydrogenations of carbon–carbon double bonds were less efficient with Pt. On the other hand, slightly higher current efficiencies

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(10) Carbon felt (20 × 20 × 10 mm) (RVC 4000, 0.1 g cm^{-3}, purchased from le Carbone Lorraine) electrodes were derivatized as described previously,[9b] by controlled potential oxidation at 1.1 V vs SCE in a 0.1 M *n*-Bu_4NClO_4/CH_3CN solution containing 2 mM of I. The electropolymerization was continued until 2–4 × 10^{-5} mol of viologen units have been deposited.

(11) Perchlorate counterions of the C/(polyV^{2+}•$2ClO_4^-$) electrode were replaced by $PdCl_4^{2-}$ by dipping the electrode into an aqueous solution of 20 mM K_2PdCl_4 for 15 min, to yield C/(polyV^{2+}•$PdCl_4^{2-}$). The electrode was then rinsed and placed in a 0.1 M KCl solution. The potential was slowly moved to −0.7 V vs SCE where the (polyV^{2+}) is fully reduced to (poly$V^{\bullet+}$) which is capable of reducing $PdCl^{2-}$ to Pd.[7b,c] The amount of Pd contained in the C/(polyV^{2+}•$2Cl^-$•Pd) electrode was estimated from the charge passed to reduce $PdCl_4^{2-}$ to Pd. This procedure resulted in the incorporation of 2.4 × 10^{-5} mol of Pd in a film containing 3.3 × 10^{-5} mol of viologen units. The impregnation procedure was repeated once to double the amount of metal catalyst in the polymer. Incorporation of Pt and Rh were accomplished with the use of K_2PtCl_4 and Na_3RhCl_6, respectively. Incorporation of Rh appeared less efficient, and the impregnation procedure was repeated twice to obtain ~1 mol of Rh per mol of viologen units.

(12) Supporting electrolyte was 0.1 M KCl or K_2SO_4; pH 1–2 was established by addition of HCl or H_2SO_4.

(13) Ethanol or 2-ethoxyethanol was often added to aid dissolution of water insoluble substrates; pH 1 was maintained by continuous addition of acid.

(14) The carbon-felt electrode was plated at 0 V in a 10^{-2} M K_2PdCl_4 aqueous solution. The quantity of electricity passed (9.6 C) was the theoretical quantity required for deposit 5 × 10^{-5} mol of Pd.

(15) First, the carbon-felt electrode was coated by a thin polypyrrole film by controlled potential oxidation (18.5 C) at 1 V vs SCE in a 0.1 M Et_4NClO_4/CH_3CN solution containing 6 mM of pyrrole. The procedure for Pd (around 5 × 10^{-5} mol) incorporation was similar to that used with the Cf/polyV^{2+} electrode, except that the Cf/polypyrrole electrode was potentiostated at 0.35 V vs SCE in the K_2PdCl_4 aqueous solution to allow doping of the polypyrrole film by $PdCl_4^{2-}$ ions.

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were obtained with Rh than with Pd, even with lower Rh loading.

The high catalytic efficiency achieved with low precious metal loading and the excellent stability of these cathodes make them attractive for electrocatalytic hydrogenation of organic compounds. This work is currently being expanded to test new catalytic cathodes based on various combinations of redox polymers and metal catalysts.

Acknowledgment. We thank Professor G. Cauquis and Dr. C. Petrier for fruitful discussions.

Registry No. I, 100809-39-0; (poly$V^{2+}\cdot 2Cl^-$), 110589-61-2; (poly$V^{2+}\cdot 2ClO_4^-$), 110589-62-3; $PdCl_4^{2-}$, 14349-67-8; $PtCl_4^{2-}$, 13965-91-8; $RhCl_6^{3-}$, 21412-00-0; Pd, 7440-05-3; Pt, 7440-06-4; Rh, 7440-16-6; $PhCH{=}CHCO_2H$, 621-82-9; $PhC{\equiv}CPh$, 501-65-5; $PhNO_2$, 98-95-3; $PhCH_2CH_2CO_2H$, 501-52-0; $PhCH_2CH_2Ph$, 103-29-7; $PhNH_2$, 62-53-3; 4-isopropylcyclohex-2-en-1-one, 500-02-7; 3,5,5-trimethyl-2-cyclohexen-1-one, 78-59-1; 3-methoxybenzaldehyde, 591-31-1; 4-isopropylcyclohexanone, 5432-85-9; 3,3,5-trimethylcyclohexanone, 873-94-9; 3-methoxybenzenemethanol, 6971-51-3.

Dioxygen–Copper Reactivity: X-ray Structure and Characterization of an (Acylperoxo)dicopper Complex

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Received July 6, 1987

The interaction and subsequent reactivity of dioxygen (O_2) with copper ions is of great interest due to the importance of dioxygen binding and/or activating proteins in biological systems and the utility of copper compounds in oxidative synthetic reactions.[1-3] In this communication, we report for the first time the synthesis and *X-ray structural characterization* of an (acylperoxo)dicopper(II) complex, a derivative of a coordinated dioxygen (peroxo) copper species.

We recently described a system in which O_2 reacts reversibly with a phenoxo-bridged dicopper(I) complex, $[Cu_2(XYL–O–)]^+$ (**1**) (py = 2-pyridyl), in dichloromethane solution at low temperature to give an intensely purple ($\lambda_{max} = 505$ nm, $\epsilon = 6000$ M^{-1} cm^{-1}) colored dioxygen complex, $[Cu_2(XYL–O–)(O_2)]^+$ (**2**) ($Cu{:}O_2 = 2{:}1$) (Figure 1).[4] Resonance Raman[5] and extended X-ray absorption fine structure (EXAFS)[6] spectroscopic studies have established that **2** is best formulated as a (peroxo)dicopper(II) complex ($\nu_{O-O} = 803$ cm^{-1}, Cu···Cu = 3.31 Å). The protonated form of **2**, $[Cu_2(XYL–O–)(OOH)]^{2+}$ (**3**), can also be generated,[7] and while **3** can only be handled at low temperatures, we now report that a stable and crystalline analogue of **3**, the acylperoxo bridged dicopper(II) complex **5**, can be readily prepared by either the reaction of m-$ClC_6H_4C(O)OOH$ (MCPBA) with **4** or via the direct acylation of $[Cu_2(XYL–O–)(O_2)]^+$ (**2**) with m-$ClC_6H_4C(O)Cl$, followed by a methathesis reaction (Figure 1).

To a dry dichloromethane solution of $[Cu_2(XYL–O–)(OH)]Y_2$ (**4**)[8] ($Y = ClO_4^-$ or PF_6^-) and 2 equiv of 2,2-dimethoxypropane at −80 °C under Ar was added 1.3 equiv of MCPBA, and by addition of dry diethyl ether, a dark green precipitate was isolated. Recrystallization by slow diffusion of diethyl ether into an acetonitrile solution of the product at −20 °C afforded the complexes $[Cu_2(XYL–O–)(m\text{-}ClC_6H_4C(O)OO)]^{2+}$ (**5**) in >90% yield (Figure 1, reaction d).[9] Acylation of $[Cu_2(XYL–O–)(O_2)]^+$ (**2**) m-$ClC_6H_4C(O)Cl$ also generated complexes **5** as shown by UV–vis and IR spectroscopy (Figure 1, reaction b). $[Cu_2(XYL–O–)(m\text{-}ClC_6H_4CO)O_2)]^{2+}$ (**5**) exhibits a strong absorption at 395 nm ($\epsilon = 5500$–5900 M^{-1} cm^{-1}) and a d–d band at 650 nm ($\epsilon = 420$ M^{-1} cm^{-1}) in the UV–vis as well as a carbonyl absorption at 1745 cm^{-1} in an IR spectrum.[9]

X-ray quality crystals of $[Cu_2(XYL–O–)(m\text{-}ClC_6H_4C(O)OO)](ClO_4)_2\cdot CH_3CN$ were grown from the reaction of MCPBA with **4**, as described above, and the structure of the dication **5** is shown in Figure 2.[10,11] The structure is very similar to that already described for complexes $[Cu_2(XYL–O–)(X)]^{2+}$ ($X = OH^-$,[8,12] N_3^-,[12,13] and halide[12]), consisting of a phenoxo and X^- doubly bridged dicopper(II) species. Each Cu(II) ion is coordinated with equatorial binding to O1, O2, the amine N atom (N1, N4), one pyridyl N donor (N3, N5), and a longer axial interaction from the other pyridine donor (N2, N6) in a distorted square-based pyramidal geometry. The acylperoxo group is coordinated through O2 in a μ-1,1-fashion, occupying the position X found in the other related structures. The acylperoxo O2–O3 bond length is 1.463 (12) Å and compares with a closely structurally related (μ-1,1-hydroperoxo)dicobalt(III) complex (O–O = 1.42 Å)[14] and with distances observed in recently reported terminally bound t-$BuOO^-$–M complexes (M = Co,[15] Hf[16]). The Cu···Cu distance in **5** is 3.197 Å, ca. 0.1 Å longer than that observed in **4**. The steric effect of the bulky MCPBA unit also results in larger Cu–O–Cu angles about the Cu_2O_2 unit (109.8 (3) and 108.3 (4) compared to 102.5 (5) and 104.4 (5) in **4**).

Unlike the hydroperoxo complex $[Cu_2(XYL–O–)(OOH)]^{2+}$ (**3**), which oxygenates PPh_3 to $O{=}PPh_3$ stoichiometrically while forming the dicopper(II) product $[Cu_2(XYL–O–)(OH)]^{2+}$ (**4**),[7] the dioxygen (peroxo) complex $[Cu_2(XYL–O–)(O_2)]^+$ (**1**) does not oxidize PPh_3.[4,17] Consistent with its apparent closer relationship to the hydroperoxo complex **3**, the acylperoxo complex $[Cu_2(XYL–O–)(m\text{-}ClC_6H_4C(O)OO)]^{2+}$ (**5**) reacts with PPh_3 to give a quantitative yield of $O{=}PPh_3$ and the carboxylato complex

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(9) $[Cu_2(XYL–O–)(m\text{-}ClC_6H_4C(O)OO)](ClO_4)_2\cdot CH_3CN$: IR (Nujol) ν(CO), 1745 cm^{-1}, ν(CN), 2250 cm^{-1}. Anal. Calcd for $C_{45}H_{46}Cu_2Cl_3O_{12}N_7$: C, 48.66; H, 4.15; N, 8.83. Found: C, 48.65; H, 4.25; N, 8.70. $[Cu_2(XYL–O–)(m\text{-}ClC_6H_4C(O)OO)](PF_6)_2$: IR (Nujol) ν(CO), 1745 cm^{-1}. Anal. Calcd for $C_{43}H_{43}Cu_2ClF_{12}N_6O_4P_2$: C, 44.49; H, 3.70; N, 7.24. Found: C, 43.93; H, 3.57; N, 6.98. An unambiguous assignment for the peroxide ν(O–O) cannot be made at this time due to the presence of ligand absorptions in the 700–850-cm^{-1} region.

(10) Complex **5**-$(ClO_4)_2\cdot CH_3CN$ crystallizes in the monoclinic space group $C2/c$ with $a = 23.149$ (6) Å, $b = 13.327$ (3) Å, $c = 32.935$ (5) Å, $\beta = 97.78$ (2)°, $V = 10067$ (4) $Å^3$, and $Z = 8$. A Nicolet R3m diffractometer was used in the ω-scan mode to collect 4691 reflections of which 2459 reflections with $F_o \geq 6\ \sigma|F_o|$ were used in the solution and refinement. The positional parameters of the copper atoms were determined by the Patterson method. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were calculated and fixed at 0.96 Å from carbon; the phenyl and pyridyl rings were refined as rigid hexagons ($d(C–C(N)) = 1.395$ Å). The structure was refined to the current residual values of $R = 0.0628$ and $R_w = 0.0670$ (Mo Kα, $\lambda = 0.71073$ Å).

(11) Supplementary Material.

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(17) The reaction PPh_3 with $[Cu_2(XYL–O–)(O_2)]^+$ (**1**) at −80 °C results in the quantitative evolution of O_2 and the production of a bis(triphenylphosphine)dicopper(I) adduct complex $[Cu_2(XYL–O–)(PPh_3)_2]^+$, see ref. 4.

0002-7863/87/1509-6889$01.50/0