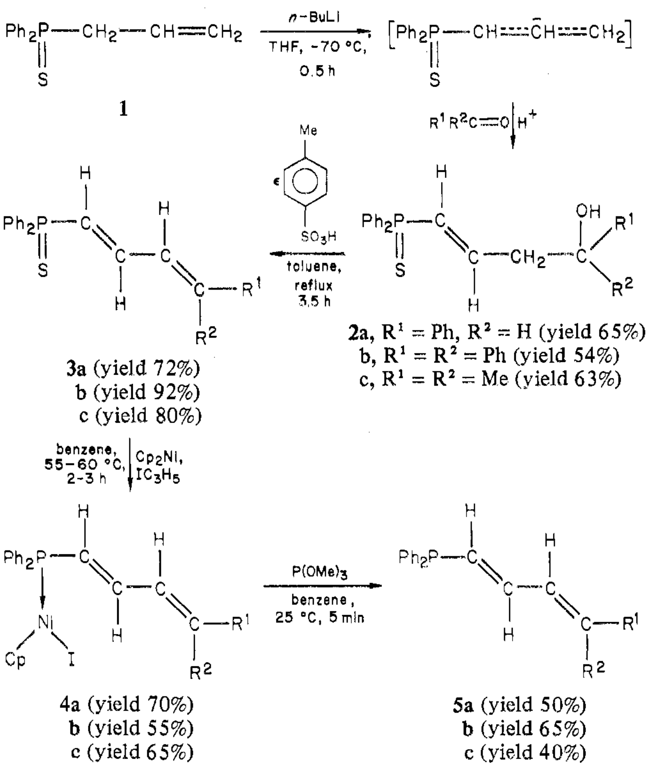
Scheme I. Synthesis of (*E*)-1,3-Butadienyldiphenylphosphines



[[[(*E*,*E*)-(η^4-4-Phenyl-1-(diphenylphosphinyl)-1,3-butadienyl)]tricarbonyliron]-*P*]tetracarbonyliron (9). (a) From 7. A mixture of complex **7** (0.3 g, 6.2×10^{-4} mol) and $Fe_3(CO)_{12}$ (0.3 g, 5.9×10^{-4} mol) in benzene (50 mL) was heated and stirred at 80 °C for 20 h in an argon atmosphere. After cooling of the solution to room temperature, the solvent was removed in vacuo. The oily residue chromatographed with hexane–benzene (60:40) gave first the starting complex **7** (0.1 g; $R_f = 0.75$) and then the orange complex **9** (0.2 g, 50%; $R_f = 0.4$).

(b) From Phosphine Sulfide. A mixture of **3a** (1 g, 3.18×10^{-3} mol) and $Fe_2(CO)_9$ (2 g, 5.49×10^{-3} mol) in toluene (50 mL) was heated and stirred at reflux in an argon atmosphere for 8 h. After cooling of the solution to room temperature, the black precipitate that formed was filtered and the solvent evaporated. The residue when chromatographed gave **7** (0.3 g, 20%) and **9** (0.2 g, 11%): IR (Nujol) 2055 (s), 2040 (m) 2010 (w), 1990 (s), 1965 (w), 1945 (s), 1905 (m) cm^{-1}; ^{31}P NMR δ +70.93; mass spectrum (70 eV, 80 °C), *m/e* 622 (13) [M], 594 (11) [M – CO], 566 (28) [M – 2CO], 538 (25) [M – 3CO], 510 (25) [M – 4CO], 482 (57) [M – 5CO], 454 (23) [M – 6CO], 426 (100) [M – 7CO], 370 (60) [M – 7CO – Fe], 314 (11) [M – 7CO – 2Fe].

[[[(*E*,*E*)-(η^4-4-Phenyl-1-(diphenylphosphinyl)-1,3-butadienyl)]tricarbonyliron]-*P*]pentacarbonylmolybdenum (10) was prepared from 0.9 g (1.63×10^{-3} mol) of **8** and 0.81 g (1.6×10^{-3} mol) of $Fe_3(CO)_{12}$ in the same way as above (procedure a). Chromatography (eluant = hexane–benzene, 90:10) gave first the starting complex **8** (0.1 g) and then complex **10**: 1 g (79%); $R_f = 0.35$; mp 102–103 °C (from pentane); IR (Nujol) 2070 (m), 2052 (m), 2000 (m), 1988 (m), 1951 (s, sh), 1945 (s) cm^{-1}; ^{31}P NMR (C_6D_6) δ +34.6; mass spectrum (70 eV, 100 °C, ^{98}Mo), *m/e* 692 (≃1) [M], 636 (≃1) [M – 2CO], 608 (3) [M – 3CO], 580 (2) [M – 4CO], 552 (2) [M –5CO], 524 (5) [M – 6CO], 496 (2) [M – 7CO], 468 (7) [M – 8CO], 412 (8) [M – Fe – 8CO], 370 (100) [M – Mo – 8CO], 314 (100) [M – Mo – Fe – 8CO].

Registry No. 1, 10061-87-7; **2a**, 73210-27-2; **2b**, 73210-28-3; **2c**, 73210-29-4; **3a**, 73210-30-7; **3b**, 73210-31-8; **3c**, 73210-32-9; **4a**, 73210-37-4; **4b**, 73210-38-5; **4c**, 73210-39-6; **5a**, 73210-33-0; **5b**, 73210-34-1; **5c**, 73210-35-2; **6**, 73210-36-3; **7**, 73210-40-9; **8**, 73210-41-0; **9**, 73210-42-1; **10**, 73210-43-2; chlorodiphenylphosphine, 1079-66-9; allyl bromide, 106-95-6; benzaldehyde, 100-52-7; benzophenone, 119-61-9; acetone, 67-64-1; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; $Mo(CO)_5THF$, 53248-43-4.

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Metal Phthalocyanine Complexes. 1. Synthesis and Properties of $[Ru(ClPC)(py)_2]\cdot 4py$ and $[Ru(ClPC)(PPh_3)_2]$

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A number of six-coordinate ruthenium(II) phthalocyanines have been prepared and are well characterized.[1-4] There has also been a report[5] of the preparation of several ruthenium(III) phthalocyanine complexes with the general formula [Ru(PC)ClL′], where L′ equals phthalonitrile or *o*-cyanobenzamide. When L′ is equal to pyridine, there are three or four additional pyridine molecules of crystallization, [Ru(PC)Cl(py)]·*n*py (*n* = 3 or 4). Elemental analyses and limited spectral and physical properties indicate, however, that the materials are not pure. Thus, we have attempted, by using the same procedure, to synthesize in a well-characterized form Ru(III) derivatives. It turns out, however, that we have synthesized Ru(II) complexes of the monochlorinated phthalocyanine macrocycle, $[Ru(ClPC)(py)_2]\cdot 4py$ and $[Ru(ClPC)(PPh_3)_2]$, in good yields (60–70%).

Experimental Section

All materials were obtained commercially and used without further purification. Infrared spectra were taken with a PE-457 spectrophotometer with the samples in a KBr disk. Electronic absorption spectra were taken with a Cary 14 spectrophotometer on benzene solutions. Magnetic susceptibility measurements on the solids at 20 °C were made with a Faraday balance at Vanderbilt University, while NMR spectra were taken with a 250-MHz spectrometer at Carnegie-Mellon University on saturated solutions of the complexes in deuterated dimethyl sulfoxide with Me_4Si as an internal standard. Thermal gravimetric measurements were made with a Perkin-Elmer TGA apparatus. The solid samples were placed in a N_2 stream (100 mL/min) and heated (10 °C/min) from ambient temperature to 900 °C, and the weight loss was recorded. Elemental analyses were done by Dornes U. Kolbe, Mulheim, West Germany.

$[Ru(ClPC)(py)_2]\cdot 4py$. An intimate mixture of the solids *o*-dicyanobenzene, 12.8 g (0.10 mol), and 2.6 g (0.01 mol) of $RuCl_3\cdot 3H_2O$ is made by grinding the materials thoroughly together in a mortar and pestle. The gray solid is heated in a 50-mL round-bottom flask fitted with an air condenser at 280 °C for 4 h. The resulting blue-black solid is cooled and transferred to a funnel. Extraction of the material with 5 × 50 mL of boiling distilled water removes excess *o*-dicyanobenzene. The remaining solid is transferred to a thimble which is placed in a Soxhlet extractor. Extraction with 150 mL of methanol is carried out for 48 h. At this point, the methanol solution in the extractor is light blue, while the flask contains a dark green solution. The methanol extract contains various hydrolysis products of *o*-dicyanobenzene and its trimer, 2,4,6-tris(*o*-cyanophenyl)-1,3,5-triazine. The solid is then extracted, in the same apparatus, with 150 mL of pyridine for 2 weeks. At the end of this time, the pyridine in the extractor is faintly blue while the pyridine in the flask is dark blue. The black residue left in the thimble amounts only to 0.3 g. The pyridine extract is evaporated to dryness in air to yield a red-violet solid; yield 7.2 g, 68% based on the ruthenium used. Anal. Calcd

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for $C_{62}H_{45}H_{14}ClRu$ (mol wt 1123): C, 66.3; H, 4.0; N, 17.4; Ru, 9.0; Cl, 3.2. Found: C, 66.0; H, 3.6; N, 17.9; Ru, 9.3; Cl, 3.2. Spectral properties: IR bands 1490, 1437, 1416, 1329, 1291, 1172, 1126, 1069, 754, 736, 695 cm^{-1}; electronic absorption bands 1.60 μm^{-1} ($\epsilon = 5.9 \times 10^4$), 1.8 μm^{-1} (shoulder), 2.66 μm^{-1} (1.3×10^4), 31.5 μm^{-1} (7.9×10^4); NMR lines (ppm) [PC] −9.30, −9.28, −9.27, −9.26, −9.24, −9.23, −9.21, −9.20, −9.19, −8.13, −8.12, −8.11, −8.10, −8.08, −8.06, −8.04, [py(free)] −7.60 (γ), −7.20 (β), −8.64 (α), [py(coordinated)] −5.82 (γ) (the lines for β and α protons are obscured by solvent resonances); magnetic moment, $\chi_m = -700 \times 10^{-6}$ cgsu, calculated diamagnetic correction[6] -740×10^{-6} cgsu and $\chi_m' = 0$.

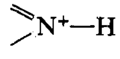
[Ru(ClPC)(PPh$_3$).2]. The complex $[Ru(ClPC)(py)_2]\cdot 4py$, 2.00 g ($1.8 \times 10^{-3}$ mol), and triphenylphosphine, 5.0 g (2.1×10^{-2} mol), are refluxed in 300 mL of xylene for 24 h. The cooled reaction mixture is filtered to remove small amounts of the trimer and metal-free phthalocyanine. The xylene solution is evaporated to dryness in an air stream. The remaining blue residue is extracted slowly with 5 × 10 mL of methanol to remove the excess triphenylphosphine and some additional trimer. The resulting solid is dissolved in 500 mL of hot benzene and the solution filtered. The benzene is removed in an air stream to yield blue crystals of a benzene solvate. Heating at 140 °C in vacuo removes the benzene. The yield was 1.4 g, 70% based on ruthenium used. Anal. Calcd for $C_{68}H_{45}N_8P_2ClRu$ (mol wt 1173): C, 69.5; H, 4.0; N, 9.5; P, 5.3; Ru, 8.6; Cl 3.0. Found: C, 69.4; H, 4.4; N, 9.8; P, 5.3; Ru, 8.6; Cl, 3.0. Spectral properties: IR bands, same frequencies as for $[Ru(ClPC)(py)_2]\cdot 4py$ with additional PPh_3 bands at 3060, 1457, 523 cm^{-1}; electronic absorption bands 1.05 μm^{-1} ($\epsilon = 1.4 \times 10^3$), 1.56 μm^{-1} (3.2×10^4), 1.7 μm^{-1} (shoulder), 2.5 μm^{-1} (shoulder), 3.3 μm^{-1} (6×10^4); NMR lines (ppm) [PC] −9.82, −9.81, −9.80, −9.78, −8.78, −8.76, −8.75, −8.74, −8.62, −8.60, −8.58, [PPh_3] −8.16; magnetic moment, $\chi_m = -760 \times 10^{-6}$ cgsu, calculated diamagnetic correction[6] -780×10^{-6} cgsu and $\chi_m' = 0$.

Results and Discussion

The red microcrystalline $[Ru(ClPC)(py)_2]\cdot 4py$ and the blue powder $[Ru(ClPC)(PPh_3)_2]$ have been characterized by total elemental analyses which unequivocally show the presence of all the constituent parts. For the former complex, the six pyridine molecules have been divided into two types: two that are axially coordinated to the metal and four that are situated in the solid lattice. Assigning two of the pyridines to axial coordination positions is reasonable since the six-coordinate structure, like $[Ru(PC)(py)_2]$, is quite pervasive.[2] Further, the presence of lattice donor molecules like pyridine or aniline is quite common in metallophthalocyanine chemistry.[3] Six-coordinate bis(phosphine) complexes of [Fe(PC)] are known, so the formulation for the latter complex is reasonable.[7]

The physical properties of the compounds are consistent with their formulation as Ru(II) complexes. They are diamagnetic and have a corrected magnetic susceptibility of zero. This is expected for a low-spin, d^6, pseudooctahedral Ru(II) complex. Further, the proton magnetic resonance spectra show multiple lines in the range −7.5 to −10.0 ppm seen for diamagnetic metallophthalocyanines and have patterns that can be assigned to α and β benz protons.[2,8] The electronic absorption spectra of the complexes show the normal strong ligand absorptions in the visible region. In addition, the infrared spectra display the normal bands for metallophthalocyanines.[9] Both the electronic and vibrational spectra of the complexes give the patterns expected for PC^{2-} and are not consistent with the presence of an oxidized macrocycle.[10]

The formation of a chlorinated phthalocyanine, as proposed here, can occur in the high-temperature synthesis of metallophthalocyanines by reaction of some metal halides and excess phthalonitrile. For example, [Pd(ClPC)] and [Cu(ClPC)] are well-known However, another possibility for the presence of one chlorine per macrocycle in the Ru(II) compounds is that the complexes are HCl adducts; i.e., the proton is bound to an aza nitrogen



and the chloride ion could be bound to the central metal atom in an axial coordination position. There is precedence for this in [Fe(PC)] chemistry, and the formation of an analogous adduct occurs for [Ru(PC)] in concentrated H_2SO_4.[12] The tightly bound nature of chlorine in the complexes argues against their formulation as HCl adducts. For one, the solids do not lose weight (HCl) when heated in the absence of air up to 250 °C. While thermally stable, the $[Fe(PC)]\cdot HCl$ adduct persists at only much lower temperatures.[13] A second point is that the complexes can be chromatographed on silica or alumina, and the recovered materials still have one chlorine atom per phthalocyanine macrocycle. Third, addition of strong base in methanol or extraction of a benzene solution with an aqueous solution (1.0 N NaOH) does not lead to a change in the visible absorption spectrum of the complexes. On the other hand, $[Fe(PC)]\cdot HCl$ shows a substantial shift of the visible absorption maxima when the HCl adduct is dissociated.[14] Finally, refluxing of the complexes in ethanol with a tenfold excess of silver nitrate for 16 h does not yield a precipitate of silver chloride.

The proton NMR spectra of the complexes are consistent with the existence of a monochlorinated macrocycle. The presence of a chloro substituent in either the α or β position of one of the benz rings destroys the fourfold symmetry of the molecule. Thus, the benz rings are no longer equivalent, and more than one set of resonances of the characteristic AA′BB′ pattern[8] should be seen in the NMR spectrum. This is the case for both complexes. The spectra show two groupings of the expected 4 lines each (pair of doublets), one group centered at −9.29 ppm and the other at −8.27 ppm for $[Ru(ClPC)(py)_2]\cdot 4py$ and one group centered at −9.80 ppm and the other at −8.76 ppm for $[Ru(ClPC)(PPh_3)_2]$. In addition, two sets of lines of half the intensity, which are seen at slightly higher fields, can be assigned to the other, nonequivalent benz ring protons.

The complexes, $[Ru(ClPC)(py)_2]\cdot 4py$ and $[Ru(ClPC)(PPh_3)_2]$, do not readily react with ligands at room temperature. For example, excess PPh_3 or py does not displace the axially bound ligands in 1 week's time. However, at elevated temperature, the substitution reaction can be effected in several hours. Thus, the complexes of Ru(II) phthalocyanine appear to be inert. The ligand-exchange reactions of the axial donor molecules appear to be quite slow, although photochemical labilization is observed.[2] These results are in marked contrast to those for $[Fe(PC)L_2]$ where the reactions are rapid and require of the order of minutes at room temperature.[15] Unlike most metallophthalocyanines $[Ru(ClPC)(py)_2]\cdot 4py$ and $[Ru(ClPC)(PPh_3)_2]$ are soluble, to the extent of several millimolar, in methylene chloride, chloroform, benzene, Me_2SO, or DMF, giving deep blue solutions. They are less soluble in acetone and alcohols and insoluble in water. Surprisingly, the compounds can also be chromatographed on silica or alumina, and their purity easily assayed by TLC by using benzene as eluant.

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The complexes [Ru(ClPC)(py)$_2$]·4py and [Ru(ClPC)(PPh$_3$)$_2$] show good thermal stability in the absence of air. The compounds can be dried in vacuo or air at 110 °C without weight loss. In the range 200–400 °C, however, the solids decompose in air to yield, among other things, metal-free phthalocyanine and RuO$_2$. On the other hand, thermal gravimetric measurements show that in an N$_2$ stream neither complex shows weight loss up to 250 °C. The complex [Ru(ClPC)(py)$_2$]·4py starts to lose weight at 360 °C, and this continues to 420 °C where the TGA trace levels off. The weight loss (22% observed, 21% calculated) corresponds to reaction 1.

$$[\mathrm{Ru(ClPC)(py)_2}]\cdot 4\mathrm{py} \xrightarrow{360\text{–}420\ ^\circ\mathrm{C}} [\mathrm{Ru(ClPC)(py)_2}]\cdot\mathrm{py} + 3\mathrm{py} \quad (1)$$

For [Ru(ClPC)(PPh$_3$)$_2$], the solids start to lose weight at 280 °C and this continues to 340 °C. The next weight loss starts at 370 °C and finishes at 440 °C. The weight losses (22% observed, 23% calculated and 21% observed, 23% calculated) correspond to reactions 2 and 3.

$$[\mathrm{Ru(ClPC)(PPh_3)_2}] \xrightarrow{280\text{–}340\ ^\circ\mathrm{C}} [\mathrm{Ru(ClPC)PPh_3}] + \mathrm{PPh_3} \quad (2)$$

$$[\mathrm{Ru(ClPC)(PPh_3)}] \xrightarrow{370\text{–}440\ ^\circ\mathrm{C}} [\mathrm{Ru(ClPC)}] + \mathrm{PPh_3} \quad (3)$$

It is interesting to note that syntheses of Ru(II) phthalocyanines have been detailed that involve the high-temperature, 280–300 °C, reaction of excess phthalonitrile and RuCl$_3$·3H$_2$O. As shown here, the procedure yields [Ru(ClPC)] as the major product. The chlorination activity of the reaction mixture may arise from the formation of chlorine in the thermal reduction of RuCl$_3$ to yield a lower oxidation state species which then undergoes a redox condensation reaction with phthalonitrile to form [Ru(PC)]. Subsequent chlorination to give [Ru(ClPC)] is most likely since chlorination of phthalonitrile prior to condensation should lead to several polychlorinated macrocycles instead of the high yield of monochlorinated phthalocyanine. In the presence of naphthalene the reaction of RuCl$_3$·3H$_2$O and excess *o*-cyanobenzamide gives [Ru(PC)] although in low yield.[2] In this case the chlorination of naphthalene may occur in preference to that of the phthalocyanine. Further, when the high-temperature synthesis is carried out with a reducing atmosphere of CO, the product is exclusively [Ru(PC)CO].[4] In this case the CO reduces the Ru(III) to a Ru(0) carbonyl which is then involved in the redox condensation reaction with phthalonitrile. No chlorination occurs since RuCl$_3$ does not undergo thermal reduction.

Finally, this work has not been able to establish unequivocally the existence of a Ru(III) phthalocyanine complex. We have shown that, with use of the procedure of Keen and Malerbi,[5] the major product isolated after suitable workup is a Ru(II) complex of the chlorinated PC macrocycle [Ru(ClPC)(py)$_2$]·4py. This corresponds to the Keen and Malerbi product [Ru(PC)Cl]·*n*py (*n* = 4 to 5).[5] We have not studied the first product of their procedure, [Ru(PC)Cl]·C$_6$H$_4$(CN)$_2$, which is later converted to the pyridine complex. Thus, we cannot say whether it is a Ru(III) complex or not. It should be pointed out, however, that the elemental analysis of this compound is in poor agreement with the proposed formulation; e.g., percent C found is low by 4.7% (absolute). Further, the magnetic moment of the material is low for a Ru(III) compound. All in all, it is reasonable to suggest that the isolated product is a mixture of several materials and not a pure compound. In fact, the method of purification which only utilizes acetone extraction of the reaction mixture to remove soluble impurities would not be expected to yield a pure material.

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Oxygen-17 Nuclear Magnetic Resonance Spectroscopy of Certain Molybdenum(IV) and Dinuclear Molybdenum(V) Complexes

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The sensitivity of the ^{17}O chemical shift of ligated oxygen atoms to metal–oxygen bond multiplicity has been established for several classes of metal–oxo compounds.[1,2] In a recent study of mononuclear oxomolybdenum(VI) complexes, we have shown that bond distances, stretching force constants, and estimated π-bond orders for a series of MoO bonds are directly related to the ^{17}O chemical shifts of the oxo ligands.[3] Oxo ligands are also prevalent in the coordination chemistries of Mo(V) and, to a lesser degree, Mo(IV). We have examined the ^{17}O NMR spectra of several of these complexes to determine the extent of similar correlations for the lower oxidation states and the effect of the oxidation state upon the chemical shift of the ^{17}O resonances. The compounds which we have examined were chosen because they have been of recent chemical interest to us.

Experimental Section

The Mo(VI) complexes MoO$_2$(acac)$_2$ (acac = acetylacetonate), MoO$_2$(Etcys)$_2$ (Etcys = ethyl ester of cysteinate), and MoO$_2$(Et$_2$dtc)$_2$ (Et$_2$dtc = diethyldithiocarbamate) were isotopically enriched in ^{17}O as previously described[3] and used as starting materials for the preparation of lower oxidation state complexes. Reduction of MoO$_2$(acac)$_2$ with excess diethyldithiophosphoric acid (Et$_2$dtpH) provided samples of Mo$_2$O$_3$(Et$_2$dtp)$_4$.[4] Reduction of MoO$_2$(Et$_2$dtc)$_2$, Mo$_2$O$_3$(Et$_2$dtp)$_4$, and MoO$_2$(Etcys)$_2$ with triphenylphosphine led to MoO(Et$_2$dtc)$_2$, MoO(Et$_2$dtp)$_2$, and Mo$_2$O$_3$(Etcys)$_4$, respectively.[4,5] A solution of Mo$_2$O$_3$(Et$_2$dtc)$_4$ was generated by the rapid reaction of a 1:1 mixture of enriched samples of MoO$_2$(Et$_2$dtc)$_2$ and MoO(Et$_2$dtc)$_2$. Condensation of the Etcys ligands of Mo$_2$O$_3$(Etcys)$_4$ with acetone (previously equilibrated with enriched water) was used to prepare Mo$_2$O$_4$(Etcys)$_2$.[6] All syntheses were confirmed by infrared spectroscopy. Solutions of Mo$_2$O$_3$(Et$_2$dtc)$_4$, MoO(Et$_2$dtc)$_2$, and MoO(Et$_2$dtp)$_2$ were prepared anaerobically. Instrumentation and instrumental methods were identical with those described previously.[3] The chemical shifts and line widths of the ^{17}O NMR resonances as well as the enrichment levels and solvents are given in Table I.

Discussion of Results

As shown in Table II, the ^{17}O NMR chemical shifts of the Mo(V) complexes fall into two groups: one located between 850 and 978 ppm and the other between 530 and 612 ppm. The results of previous work[1,2] suggest that the former should be assigned to terminal oxo ligands while the latter are due to this ligand in bridging sites. This assignment finds further support in the spectra of those complexes containing the Mo$_2$O$_3$ moiety, since the resonances in the vicinity of 900 ppm are more intense than those near 500 ppm. The Mo(IV) complexes, containing only one terminally bound oxo ligand, have resonances at 820 and 842 ppm. The terminal and bridging stretching frequencies and the corresponding MoO bond

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