

(CO)₅(4-CNpyr), and Mo(CO)₅(4-FMpyr) in benzene at room temperature are summarized in Table I. The electronic absorption spectrum obtained from a 10⁻⁴ M solution of Mo(CO)₅(4-BNpyr) in benzene is shown in Figure 1. Preliminary results have indicated that for each complex, the band maximum at 392-394 nm is relatively unaffected by changes in solvent, whereas the shoulder in the 430-450-nm region is affected both in intensity and position by the nature of the solvent.

The emission and excitation spectra recorded from deaerated,¹³ filtered¹² solutions of Mo(CO)₅(4-ACpyr), Mo(CO)₅(4-BNpyr), Mo(CO)₅(4-CNpyr), and Mo(CO)₅(4-FMpyr) in benzene at room temperature were corrected for variation in instrumental response as a function of wavelength. The emission spectrum of 10⁻⁴ M Mo(CO)₅(4-BNpyr) in benzene is shown in Figure 1; the emission spectra obtained from the other complexes were similarly broad and unstructured and their maxima are listed in Table I. The spectral distribution of the emission was observed to be insensitive to excitation wavelengths longer than 280 nm for each complex. Emission quantum yields were calculated for the Mo(CO)₅L complexes in benzene at room temperature by using a known emitter, Ru(bpy)₃²⁺,¹⁴ and the results are shown in Table I. The excitation spectrum of 10⁻⁴ M Mo(CO)₅(4-BNpyr) in benzene is shown in Figure 2 and shows features typical of those recorded from the Mo(CO)₅L series. Two distinct bands are observed, centered at 366 and 455 nm. Corresponding features were recorded in the excitation spectra of Mo(CO)₅(4-ACpyr) at 375 and 431 nm, of Mo(CO)₅(4-CNpyr) at 343 and 469 nm, and of Mo(CO)₅(4-FMpyr) at 358 and 470 nm, all complexes being 10⁻⁴ M in benzene.

Although the synthesis of several Mo(CO)₅L complexes has been reported,^{1,2} this appears to be the first report for the Mo(CO)₅(4-substituted pyridine) series. The pyridine derivatives of metal carbonyls can be expected to exhibit low-energy MLCT excited states due to the low oxidation states of the metal. Thus, we assign the solvent-dependent long-wavelength shoulder (430-450-nm region) in the absorption spectra of the Mo(CO)₅L complexes to be a MLCT transition. By comparing the absorption spectra of Mo(CO)₅(pyr) and Mo(CO)₅(pip) with the Mo(CO)₅L complexes,¹⁵ it is found that the strongly electron-withdrawing substituents yield substantially lower energy MLCT absorptions. Large substituent and solvent effects on the energy of the MLCT transition have been observed in the electronic absorption spectra of isoelectronic W(CO)₅L^{3b,5b} and Ru(NH₃)₅L²⁺¹⁶ complexes. The absorption band at 392-394 nm for the Mo(CO)₅L complexes is relatively insensitive to changes in the nature of ligand substituent and solvent medium. These absorptions are assigned to be due to a ligand field (LF) transition, in agreement with those reported for related carbonyl complexes.²⁻⁵ The use of spin multiplicity designations has been avoided in these assignments because there is expected to be substantial coupling of spin and orbit angular momenta for the Mo(CO)₅L complexes. Studies are in progress to gain further information about the character of the excited states of Mo(CO)₅L by using band analysis and MCD spectroscopy. Recent MCD analyses of the electronic excited states of M(CO)₅L complexes, where M = Cr, Mo, or W and L = N or P donor, have appeared in the literature.^{17,18}

Broad, unstructured emission with quantum yields of the order of 10⁻⁴-10⁻³ was observed from the Mo(CO)₅L complexes following excitation in room-temperature solution. A particularly novel aspect of these Mo(CO)₅L complexes is that they appear to represent the first class of second-row transition-metal carbonyls known to luminesce in fluid solution. For these complexes the coupling of spin and orbital angular momenta is expected to be

considerably less than the corresponding W(CO)₅L series.¹⁹ Due to the relative positions of the bands in the absorption and emission spectra of the Mo(CO)₅L complexes, the emission is assigned to be from the low-lying MLCT excited state and is estimated to be at (19.2 ± 0.5) × 10³ cm⁻¹ for each complex. Importantly, for Mo(CO)₅(pyr), in which the lowest excited state is a LF one,⁹ we were unable to observe emission in room-temperature solution.

The excitation and absorption spectra of Mo(CO)₅(4-BNpyr) under identical conditions are not congruent, indicating a wavelength dependence for φ_e. The most intense band at 455 nm is assigned to the MLCT emitting state. The excitation spectrum shows a minimum at 398 nm, close to that of the LF absorption. This result implies that the LF excited state does not efficiently populate the emitting state but that its energy degradation is by an alternative route. The LF excited state may be a reactive one; it has been attributed to be reactive for W(CO)₅L,^{3b} W(CO)₄L₂,^{3d} and Ru(NH₃)₅L²⁺,^{16a} complexes. The excitation band at 366 nm suggests the presence of an excited state, lying above the LF one, which can effectively populate the emitting state.

The lack of available data for the radiative and nonradiative processes has, up to the present time, inhibited models for the excited states of the group 6B metal carbonyls and their derivatives. We hope through temperature, solvent, and quenching studies to obtain detailed knowledge about the excited states of Mo(CO)₅L and related complexes and to explore the possibility of excited-state tuning.^{16b,20}

Acknowledgment. We are grateful to Professor Leslie M. Loew for use of the spectrofluorimeter and to Mary Bridge for technical assistance.

Registry No. Mo(CO)₅(4-ACpyr), 80925-81-1; Mo(CO)₅(4-BNpyr), 80925-82-2; Mo(CO)₅(4-CNpyr), 80925-83-3; Mo(CO)₅(4-FMpyr), 80925-84-4.

(19) Moore, C. E. "National Standards Reference Data Service"; National Bureau of Standards: Washington, D.C., 1971; Vol. 3.

(20) (a) Crosby, G. A.; Watts, R. J.; Carstens, D. H. W. *Science (Washington, D.C.)* **1970**, *170*, 1195-1196. (b) Watts, R. J.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 3184-3188.

Karachine: An Unusual Protoberberine Alkaloid

Gábor Blaskó,¹ Natesan Murugesan, Alan J. Freyer, and Maurice Shamma*

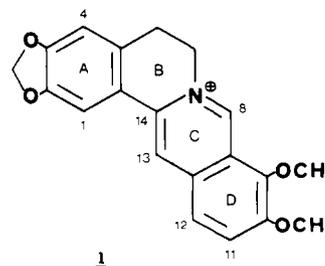
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Akber Ali Ansari and Atta-ur-Rahman*

H. E. J. Postgraduate Institute of Chemistry
University of Karachi, Karachi 32, Pakistan

Received June 15, 1981

We describe the isolation and characterization of karachine (2),



(13) As oxygen quenching was observable, the solutions were purged with Ar for 20 min prior to taking measurements.

(14) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853-4858.

(15) Darenbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959-966.

(16) (a) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 601-603.

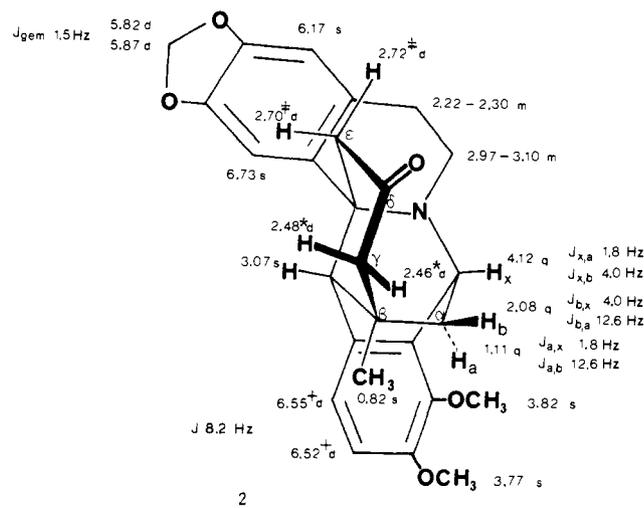
(b) Ford, P. C. *Revs. Chem. Intermed.* **1979**, *2*, 267-296.

(17) Schreiner, A. F.; Amer, S.; Duncan, W. M.; Ober, G.; Dahlgren, R. M.; Zink, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 6871-6872.

(18) Boxhoorn, G.; Stufkens, D. J.; van de Coolwijk, P. J. F. M.; Heze-mans, A. M. F. *Inorg. Chem.* **1981**, *20*, 2778-2782.

the first naturally occurring berbinoid incorporating acetone units and undoubtedly the most complex of the more than 50 protoberberine alkaloids presently known.

(1) Permanent address: Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1025 Budapest, Hungary.



J_{gem} for γ -c and ϵ -c methylene protons = 14.0 and 14.3 Hz, respectively; chemical shift values with identical superscripts are interchangeable

Berberis aristata DC (Berberidaceae) is a shrub found in the northern mountainous regions of Pakistan and India, as well as in the Nilgiri Hills of southern India. The extracts, made from the root bark, are known as "rasaut" and are used in the Unani system of medicine for the treatment of jaundice and skin diseases.² At least eight alkaloids are known to be present in the plant, the main one being berberine (1).³

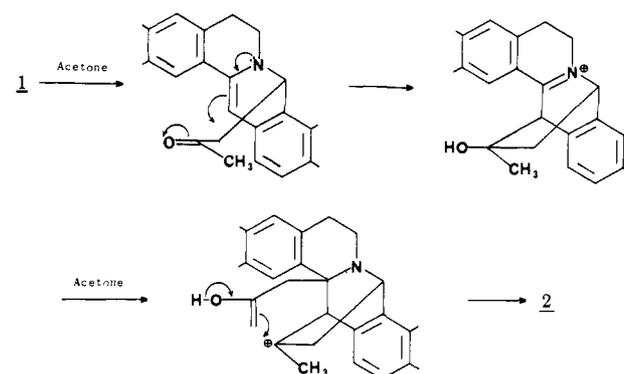
In an effort to study the minor alkaloids of *B. aristata*, 3 kg of "rasaut" were extracted with ethanol, and the basic extracts were chromatographed first over alumina and then over silica gel. A small quantity (8 mg) of the new, colorless, and optically inactive alkaloid karachine, $C_{26}H_{27}O_5N$, was thus obtained; mp 146–148 °C (ethyl acetate).

The UV spectrum, λ_{max} (EtOH) 226 (sh) and 285 nm ($\log \epsilon$ 3.90 and 3.62), was immediately suggestive of a tetrahydroprotoberberine. The mass spectrum shows a molecular ion at m/e 433 and a base peak at m/e 336. The latter peak fits exactly for the molecular ion of berberine (1) and is formed by loss of 97 mass units from the molecular ion via cleavage α to the nitrogen atom (C-14 to C- ϵ bond) followed by a retro-Diels-Alder process. The m/e 97 fragment corresponds to C_6H_5O or more specifically to 2 mol of acetone minus the elements of water.⁴ A sharp absorption band at 1710 cm^{-1} in the IR spectrum ($CHCl_3$) denotes the presence of a nonconjugated carbonyl.

The 360-MHz FT NMR spectrum in $CDCl_3$ presents a complex pattern but allows for the tentative assignment of structure 2 to karachine. This spectrum has been summarized in expression 2. Of particular diagnostic value are the protons bonded to the α -to- ϵ carbon chain, namely the one-proton quartet centered at δ 1.11 ($J_{a,x} = 1.8\text{ Hz}$, $J_{a,b} = 12.6\text{ Hz}$) due to H_a , another one-proton quartet at δ 2.08 ($J_{b,x} = 4.0\text{ Hz}$, $J_{b,a} = 12.6\text{ Hz}$) corresponding to H_b , the upfield singlet at δ 0.82 assigned to the bridgehead methyl group attached to C- β , and the two sets of two-proton doublets of doublets at δ 2.46 and 2.48 ($J_{gem} = 14.0\text{ Hz}$) and at δ 2.70 and 2.72 ($J_{gem} = 14.3\text{ Hz}$), representing the C- γ and the C- ϵ protons, respectively. Noteworthy also is the one-proton quartet at δ 4.12 ($J_{x,a} = 1.8\text{ Hz}$, $J_{x,b} = 4.0\text{ Hz}$) allocated to H-8.

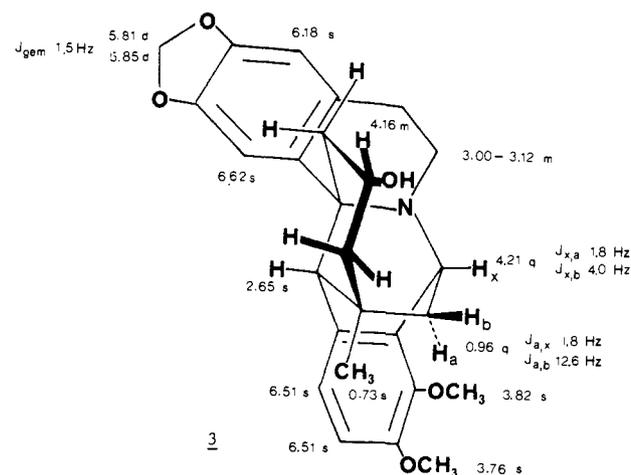
In order to settle conclusively the nature of the substitution pattern in aromatic rings A and D of karachine, a nuclear Overhauser enhancement (NOE) study was carried out. Irradiation of the C-10 methoxyl singlet at δ 3.77 resulted in an overall 11.6% increase in the area of the δ 6.52 and 6.55 ring D aromatic doublet of doublets. Alternatively, irradiation of the H-1 singlet at δ 6.73

Scheme I



gave a 2.8% increase of the δ 2.70 and 2.72 doublet of doublets assigned to the C- ϵ protons, as well as to a 5.6% increase of the signal at δ 3.07 due to H-13. Significantly, irradiation of either the H-1 or H-4 singlets at δ 6.73 and 6.17, respectively, led to no observable NOE for the methoxyl absorptions. It appears likely, therefore, that karachine (2) is formed by the condensation of berberine (1) with 2 mol of acetone and accompanying loss of water, as suggested in Scheme I.

As further confirmation of structure 2 for karachine, the alkaloid was reduced with sodium borohydride in methanol to supply amorphous dihydrokarachine (3), $C_{26}H_{29}O_5N$, in which it is as-



protons whose chemical shifts are not indicated appear as a broad multiplet δ 1.60–2.30

sumed that the reducing agent has approached from the less hindered side of the carbonyl. The mass spectrum of 3 shows a molecular ion m/e 435, and significantly the base peak m/e 336 is identical with that present in the mass spectrum of karachine (2).⁵ The 360-MHz NMR spectrum ($CDCl_3$) of dihydrokarachine, as summarized in expression 3, exhibits a three-proton upfield singlet at δ 0.73 due to the bridgehead methyl group attached to C- β . A one-proton quartet at δ 0.96 ($J_{a,x} = 1.8\text{ Hz}$, $J_{a,b} = 12.6\text{ Hz}$) can be allotted to H_a on C- α . The δ 1.60–2.30 region is blurred by a complex multiplet consisting of two ABX systems, due to the C- γ and C- ϵ protons coupled to the C- δ proton. Irradiation of the C- δ proton at δ 4.16, therefore, led to a much simpler spin-decoupled pattern of two overlapping AB systems at δ 1.67 and 2.29 ($J_{gem} = 14.0\text{ Hz}$) and δ 1.88 and 2.22 ($J_{gem} = 14.0\text{ Hz}$), ascribable to the methylene protons at C- γ and C- ϵ .

So that karachine could be ascertained to be a true alkaloid and not an artifact of isolation, the plant extraction and fractionation procedure were repeated with purified, acetone-free solvents. This led to the reisolation of the alkaloid. Inspection

(2) Chopra, R. N. "Glossary of Indian Medicinal Plants"; CSIR: New Delhi, 1956; p 36.

(3) Chatterjee, R. *J. Indian Chem. Soc.* **1951**, *28*, 225.

(4) The mass spectrum of karachine shows m/e 433 (78), 418 (19), 390 (23), 375 (4), 336 (100), 321 (27), 292 (16), 278 (21), 263 (3), 189 (21), and 174 (3).

(5) The mass spectrum of dihydrokarachine (3) shows m/e 435 (21), 420 (6), 390 (4), 336 (100), 321 (15), 292 (8), 278 (9), 263 (1), 189 (16), and 174 (2).

of the structure of karachine (**2**) indicates the degree of complexity attainable in nature starting from a relatively simple berbinoid skeleton.⁶

Acknowledgment. This project was supported by Grant CA-11450 from the National Cancer Institute, NIH, DHHS. G.B. is the recipient of an IREX fellowship. We are grateful to Theresa S. Dunne for technical assistance. A.R. and A.A.A. express their gratitude to Hakim Mohammad Said, Chairman, Hamdard National Foundation, Karachi, for providing the plant material.

Registry No. **2**, 80908-02-7; **3**, 80908-03-8.

(6) For a recent review on purely synthetic adducts of berberine with acetone, see: Govindachari, T. R.; Pai, B. R.; Rajeswari, S.; Natarajan, S.; Chandrasekaran, S.; Premila, M. S.; Charubala, R.; Venkatesan, K.; Bhadrabade, M. M.; Nagarajan, K.; Richter, W. J.; *Heterocycles* **1981**, *15*, 1463. Such adducts bear minimal structural resemblance to karachine.

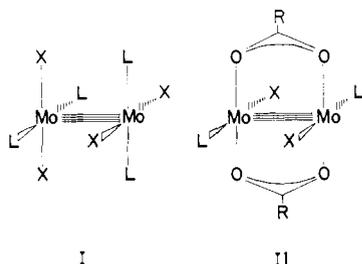
Quadruply Bonded Dimolybdenum Compounds of the Type $\text{Mo}_2(\text{O}_2\text{CR})_2\text{X}_2(\text{PR}_3)_2$: Evidence for Kinetic and Structural Trans Effects

Gregory S. Girolami, Vera V. Mainz, and Richard A. Andersen*

Department of Chemistry, University of California Berkeley, California 94720

Received October 19, 1981

It has been shown recently that the PET_3 ligands in $\text{Mo}_2\text{Me}_4(\text{PET}_3)_4$, of stereochemistry I, undergo stepwise exchange with



either PMe_3 or PMe_2Ph in toluene solution by a dissociative mechanism.¹ In this class of molecules, the phosphine ligands L are cis to the anionic groups X. An analogous study of binuclear compounds in which the phosphines are trans to the anionic groups was of interest. The bis(carboxylato) complexes of stereochemistry II are well suited for such a study.²⁻⁴ We now present kinetic, crystallographic, and spectroscopic data as a function of the anionic group, X, which provide the first evidence for both kinetic and structural trans effects operating in quadruply bonded dimers.

The red siloxide derivative $\text{Mo}_2(\text{O}_2\text{CCMe}_3)_2(\text{OSiMe}_3)_2(\text{PMe}_3)_2^5$ can be prepared from $\text{Mo}_2(\text{O}_2\text{CCMe}_3)_4$, LiOSiMe_3 , and PMe_3 in diethyl ether, followed by crystallization from pentane at -10°C . The NMR parameters indicate a structure of type II, and this was confirmed by an X-ray crystallographic study (see Figure 1).⁶ The structure has two independent half-molecules in the

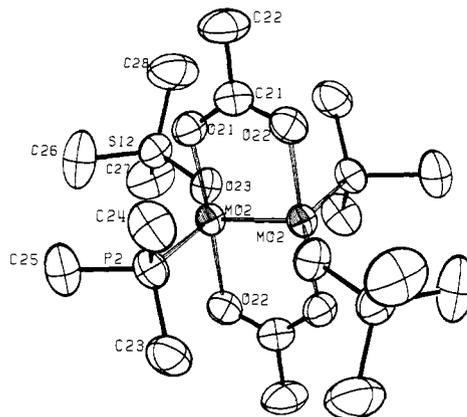


Figure 1. ORTEP view of $\text{Mo}_2(\text{O}_2\text{CMe})_2(\text{OSiMe}_3)_2(\text{PMe}_3)_2$. Important bond lengths and angles: $\text{Mo}-\text{Mo} = 2.114(1) \text{ \AA}$, $\text{Mo}-\text{O}(\text{siloxide}) = 2.019(9) \text{ \AA}$, $\text{Mo}-\text{O}(\text{acetate}) = 2.11(1) \text{ \AA}$, $\text{Mo}-\text{Mo}-\text{P} = 94.02(3)^\circ$, $\text{Mo}-\text{Mo}-\text{O}(\text{siloxide}) = 116.9(5)^\circ$, $\text{P}-\text{Mo}-\text{O}(\text{siloxide}) = 149.0(5)^\circ$.

Table I. Magnitudes of $^3J_{\text{PP}}$ in the Compounds $\text{Mo}_2(\text{O}_2\text{CCMe}_3)_2\text{X}_2(\text{PMe}_2\text{Et})(\text{PMe}_3)$

X	$^3J_{\text{PP}}$, Hz	X	$^3J_{\text{PP}}$, Hz
CH_2CMe_3	4	Cl	25
CH_2SiMe_3	6	Br	29
Me	6	$\text{N}(\text{SiMe}_2\text{H})_2$	33
I	20	OSiMe_3	39

asymmetric unit. Each molecule contains a crystallographic inversion center, and each molecule possesses nearly C_{2h} symmetry, though the siloxide SiMe_3 groups are rotated slightly out of the $\text{Mo}_2\text{O}_2\text{P}_2$ plane, giving $\text{Mo}-\text{Mo}-\text{O}-\text{Si}$ torsion angles of 166.0 and 145.6° for the two independent molecules in the unit cell. The overall geometry is similar to that found in the electronically and sterically equivalent alkyl derivative $\text{Mo}_2(\text{O}_2\text{CMe})_2(\text{CH}_2\text{SiMe}_3)_2(\text{PMe}_3)_2$.⁷ The most notable difference between the two structures occurs in the $\text{Mo}-\text{P}$ distances: $2.547(1) \text{ \AA}$ in the alkyl and $2.487(1) \text{ \AA}$ in the siloxide. This difference is most reasonably ascribed to the low position of siloxide ligands relative to alkyls on the trans-influence series, which agrees with the order deduced in square-planar $\text{Pt}(\text{II})$ chemistry.⁸

In our initial attempts to study the phosphine substitution kinetics, we found that the exchange rates in the series $\text{Mo}_2(\text{O}_2\text{CCMe}_3)_2\text{X}_2(\text{PET}_3)_2$ where X is alkyl, halide, amide, or siloxide were too rapid to be followed conveniently by $^{31}\text{P}\{\text{H}\}$ NMR spectroscopy.⁹ Since kinetics studies in the $\text{Mo}_2\text{Me}_4(\text{PR}_3)_4$ system showed that smaller phosphines exhibit slower rates,¹ we prepared the series $\text{Mo}_2(\text{O}_2\text{CCMe}_3)_2\text{X}_2(\text{PMe}_2\text{Et})_2$.¹⁰ These compounds

(6) Single crystals of $\text{Mo}_2(\text{O}_2\text{CMe})_2(\text{OSiMe}_3)_2(\text{PMe}_3)_2$ are triclinic, space group $P\bar{1}$, with $a = 11.465(2) \text{ \AA}$, $b = 11.544(1) \text{ \AA}$, $c = 13.695(2) \text{ \AA}$, $\alpha = 70.54(1)^\circ$, $\beta = 64.12(1)^\circ$, $\gamma = 77.54(1)^\circ$, $V = 1532.4(3) \text{ \AA}^3$; $Z = 2$. X-ray diffraction data were collected for 4015 independent reflections having $2\theta < 45^\circ$ on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation and $\theta-2\theta$ scans. The structure was solved by the heavy-atom method. The final residuals for 254 variables refined against the 3564 data for which $F^2 > 3\sigma(F^2)$ were $R_F = 2.29\%$, $R_{wF} = 4.22\%$, and $\text{GOF} = 2.23$. In the last cycle, hydrogen atom positions were predicted and included in the structure factor calculations, but not refined.

(7) Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr. Sect. B* **1979**, *B35*, 2709-2712.

(8) *cis*- $\text{Pt}(\text{OSiMe}_3)_2(\text{PMe}_3)_2$ has $^1J_{\text{Pt-P}} = 3400 \text{ Hz}$,^{8a} while *cis*- $\text{Pt}(\text{CH}_2\text{SiMe}_3)_2(\text{PMe}_2\text{Ph})_2$ has $^1J_{\text{Pt-P}} = 1999 \text{ Hz}$,^{8b} showing that $\text{CH}_2\text{SiMe}_3 > \text{OSiMe}_3$ on a trans series. (a) Schmidbauer, H.; Adlkofer, J. *Chem. Ber.* **1974**, *107*, 3680-3683. (b) Cardin, C. J.; Cardin, D. J.; Lappert, M. F.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1978**, 46-50. For general references on trans-influence series, see: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335-422. Manojlovic-Muir, L.; Muir, K. W. *Inorg. Chim. Acta* **1974**, *10*, 47-49.

(9) The pivalate derivatives were used since they are more soluble in toluene at low temperature than their corresponding acetate analogues. Rate studies have shown that phosphine-exchange rates for the neopentyl derivatives $\text{Mo}_2(\text{O}_2\text{CR})_2(\text{CH}_2\text{CMe}_3)_2(\text{PMe}_2\text{Et})_2$ are independent of the carboxylate group ($\text{R} = \text{Me}$, CF_3 , or CMe_3).

(1) Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 3953-3955.

(2) Andersen, R. A.; Jones, R. A.; Wilkinson, G. J. *Chem. Soc., Dalton Trans.* **1978**, 446-453.

(3) Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 2165-2168.

(4) Arenivar, J. D.; Mainz, V. V.; Ruben, H.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.*, in press.

(5) Anal. Calcd: C, 30.0; H, 6.61. Found: C, 30.3; H, 6.66. Mp $157-158^\circ\text{C}$; ^1H NMR ($\text{PhH}-d_6$, 25°C) δ 2.63 (O_2CMe , s), 1.28 (PMe_3 , $\text{AA}'\text{X}_9\text{X}'_9$, $^2J_{\text{AX}} + ^3J_{\text{AX}} = 9 \text{ Hz}$), 0.20 (OSiMe_3 , s); ^{13}C [^1H] NMR ($\text{PhH}-d_6$, 20°C) δ 183.4 (O_2CMe , s), 23.2 (O_2CMe , s), 11.9 (PMe_3 , ABX, $^1J_{\text{AX}} + ^4J_{\text{BX}} = 26 \text{ Hz}$), 4.1 (OSiMe_3 , s); $^{31}\text{P}\{\text{H}\}$ NMR ($\text{PhH}-d_6$, 25°C) δ 5.0, s.