

**Figure 2.** Normalized polar angle distribution of molecular ion yields for 4.5-langmuirs pyridine (—,  $(M + H)^+$ ), 0.15-langmuirs pyridine (---,  $(M + H)^+$ ), and 2.5-langmuirs benzene (···,  $(M - H)^+$ ) on Ag(111) at 153 K.

taneously by the electron-beam-retarding field method exhibits a continuous decrease through this exposure region. The details of this behavior are illustrated in Figure 1 for the  $AgC_5H_5N^+$  and  $C_5H_5NH^+$  positive ions during pyridine adsorption. Related ions exhibit parallel trends. Similar curves for the  $C_6H_5^+$  and  $AgC_6H_6^+$  ions obtained during benzene adsorption are shown for comparison. The drop in the molecular ion signals after the maximum at 0.2 langmuir for the pyridine case is consistent with classical dynamics calculations, which predict that a shift in orientation of the molecule from parallel to perpendicular to the surface should decrease the probability of molecular emission.<sup>6</sup>

To further substantiate the link between the ion ejection process and molecular orientation, we have measured the polar angle distribution of various ejected ions for three systems—2.5-langmuirs benzene (monolayer), 4.5-langmuirs pyridine (monolayer,  $\sigma$  bonded) and 0.15-langmuir pyridine ( $\pi$  bonded) on Ag(111). The results of these distribution measurements are illustrated in Figure 2. For monolayer benzene and for  $\pi$ -bonded pyridine where the molecules are believed to lie flat on Ag(111),<sup>7</sup> the polar angle distribution of  $(M - H)^+$  (benzene) and  $(M + H)^+$  (pyridine) are broad with a peak at  $\theta = 20^\circ$ .<sup>15</sup> At the onset of the compressional phase transition, however, the polar angle distribution of the  $C_5H_5NH^+$  ion sharpens dramatically, and the peak moves to  $\theta = 10^\circ$ .

The arrangement of atoms and molecules on surfaces has been shown to influence the angular distributions of ejected atomic and molecular species.<sup>2,16</sup> The reason for this dependence is that there is a surface channeling mechanism that forces atoms to eject along open crystallographic directions where atom-atom repulsions are at a minimum. The anisotropies have previously only been found in azimuthal angle distributions. For the case of an ordered array of molecules stacked at an inclined angle relative to the surface, however, recent computer simulations<sup>17</sup> indicate that channeling effects are more clearly observable in polar angle distributions rather than in the azimuthal angle distributions as is indicated by our experiments. If this explanation is correct, our experimental results suggest that the tilt angle of the  $\sigma$ -bonded pyridine molecule is somewhat smaller than proposed previously.<sup>7</sup> Calculations currently in progress are aimed toward determining how precisely the polar angle distribution can be related to the tilt angle of the  $\sigma$ -bonded pyridine. We find that the polar angle distribution of

$\sigma$ -bonded pyridine is unusually sharp and 1.5 times wider at high kinetic energies (6–10 eV) than at low kinetic energies (3–7 eV). Presumably, the faster moving molecules can more easily deform the channel walls during desorption.<sup>18</sup>

In conclusion, we have measured the SIMS spectra of a number of organic monolayers adsorbed on Ag(111) with the goal of obtaining a detailed understanding of the basic mechanism of ejection of the molecular clusters. The experiments were suggested by molecular dynamics calculations, which predict that the yield and angular distribution of the desorbed species should be sensitive to the orientation of the surface molecule relative to the substrate. The experimental verification of these concepts establishes a new approach for the study of the orientation of molecular systems where molecular channels influence the desorbing particle's trajectory. More important, perhaps, these results provide striking confirmation of the basic application of the classical dynamics model to the understanding of organic SIMS spectra. This confirmation is particularly satisfying in view of the approximations inherent in the classical calculations and the overall complexity of the momentum dissipation process.

**Acknowledgment.** The financial support of the National Science Foundation, The Office of Naval Research, the Air Force Office of Scientific Research, and the donors of the Petroleum Research Foundation, administered by the American Chemical Society, is greatly acknowledged. The suggestions of Barbara Garrison were, of course, central to the completion of this work.

**Registry No.** Ag, 7440-22-4; pyridine, 110-86-1; benzene, 71-43-2.

(18) This trend toward wider polar angle distributions for faster moving particles is counter to that found for atom ejection. The surface channels on single-crystal metals should be more rigid than those formed by organic molecules and are less subject to deformation.

### Redox Properties of $(CN)_8PcZn$ , a New Charge-Transfer Complex

A. Giraudeau,<sup>\*1a</sup> A. Louati,<sup>\*1a</sup> M. Gross,<sup>\*1a</sup> J. J. Andre,<sup>\*1b</sup> J. Simon,<sup>\*1b</sup> C. H. Su,<sup>\*1c</sup> and K. M. Kadish<sup>\*1c</sup>

Laboratoire d'Électrochimie et de Chimie Physique  
du Corps Solide, ERA au CNRS No. 468  
Université Louis Pasteur, 67000 Strasbourg France  
Centre de Recherches sur les Macromolécules  
CNRS, 67083 Strasbourg, France  
Department of Chemistry, University of Houston  
Houston Texas 77004  
Received January 21, 1983

According to simple Hückel theory, the lowest unoccupied molecular orbital (LUMO) of phthalocyanines has doubly degenerate  $e_g$  symmetry and can therefore accept up to four electrons in an electroreduction of the  $\pi$  ring system.<sup>2,3</sup> This reversible addition of four electrons, which has been shown experimentally,<sup>4</sup> does not occur for metalloporphyrins. Although metalloporphyrins may undergo four ring reductions in nonaqueous media, the latter two reactions at more negative potentials involve irreversible two-electron transfers with concomitant protonation.<sup>5,6</sup>

In this communication we report the formation of a stable zinc phthalocyanine tetraanion that is electrochemically generated in nonaqueous media. The starting compound is octacyano-substituted zinc phthalocyanine,  $(CN)_8PcZn$  (Figure 1), whose synthesis has been reported in the literature.<sup>7-9</sup> As seen in Figure

(15) The  $M^+$  ion signal is experimentally too small to obtain angular distributions. However, the  $(M + H)^+$  or  $(M - H)^+$  ion trajectories are expected to be similar to the  $M^+$  ion trajectory due to the small mass influence of hydrogen.

(16) S. P. Holland, B. J. Garrison, and N. Winograd, *Phys. Rev. Lett.*, **43**, 220 (1979).

(17) This effect has been seen in our recent computer simulations of ion-bombarded pyridine on Ni(001) and is discussed in detail in a paper in preparation.

(1) (a) Université Louis Pasteur. (b) Centre de Recherches sur les Macromolécules. (c) University of Houston.

(2) Linder, R. E.; Rowlands, J. R.; Hush, N. S. *Mol. Phys.* **1971**, *21*, 417.

(3) Schaffer, A. M.; Gouterman, M.; Davidson, E. R. *Theor. Chim. Acta* **1973**, *30*, 9.

(4) Clack, D. N.; Yandle, J. R. *Inorg. Chem.* **1972**, *11*, 1738.

(5) Lanese, J. G.; Wilson, G. S. *J. Electrochem. Soc.* **1972**, *119*, 1039.

(6) Peychal-Heiling, G.; Wilson, G. S. *Anal. Chem.* **1971**, *43*, 550.

(7) Wöhrle, D.; Wahl, B. *Tetrahedron Lett.* **1979**, 227.

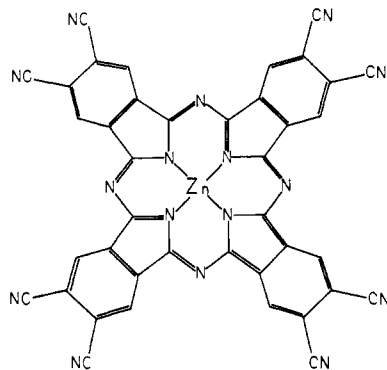


Figure 1. Structure of  $(\text{CN})_8\text{PcZn}$ .

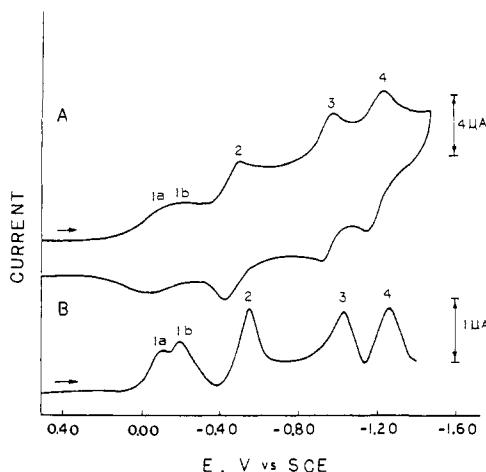


Figure 2. (A) Cyclic voltammogram of  $5 \times 10^{-4}$  M  $(\text{CN})_8\text{PcZn}$  at a Hg electrode in DMF, 0.1 M THAP; (B) differential pulse voltammogram of  $(\text{CN})_8\text{PcZn}$  at a Pt electrode in DMF, 0.1 M TBAP. Scan rate = 0.20 V/s and 10 mV/s, respectively; for DPP,  $\Delta E = 10$  mV/s.

2, electrochemical reduction of  $(\text{Pc})_8\text{PcZn}$  in DMF proceeds in five steps without destroying the phthalocyanine ring. The first two steps (labeled 1a and 1b in Figure 2) are partially overlapped by cyclic voltammetry and by differential pulse polarography and are due to an overall one-electron reduction process involving aggregated and nonaggregated  $(\text{CN})_8\text{PcZn}$ .<sup>10</sup> The currents observed by cyclic voltammetry (Figure 2A) or by differential pulse polarography (Figure 2B) for the last three steps are of equal height, indicating an identical number of electrons in each step. In addition,  $E_{pa} - E_{pc} = 60 \pm 5$  mV at low scan rates ( $v < 100$  mV/s), and  $i_p/v^{1/2}$  from the cyclic voltammograms was constant for the last three processes, indicating that one electron is reversibly transferred in each step. Coulometric measurements after each of the three processes also yield a value of  $1.0 \pm 0.05$  electrons per each electron transfer.

The EPR spectrum observed after reduction at an applied potential of  $-0.30$  V ( $g = 2.0022$ ,  $\Delta H = 5.9$  G) can be characterized as due to the radical anion  $[(\text{CN})_8\text{PcZn}]^-$ . An anion radical EPR spectrum is also generated at  $-0.10$  V vs. SCE but shows a larger line width ( $\Delta H = 13.7$  G) than the radical produced by polarization at  $-0.30$  V vs. SCE ( $\Delta H = 5.9$  G). No hyperfine structure is observed between 70 and 298 K, and one is led to the conclusion that the aggregated species, which is less mobile, is reduced before the nonaggregated species. Both types of EPR signals disappear when the diamagnetic species  $[(\text{CN})_8\text{PcZn}]^{2-}$

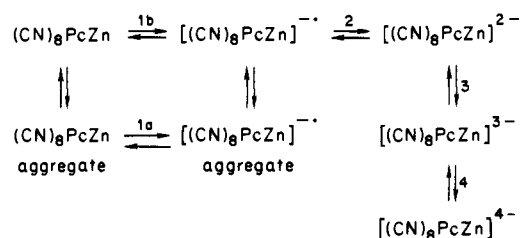
Table I. Potentials for Reduction of Zinc Phthalocyanine and Porphyrin Complexes at a Hg Electrode in DMF (0.1 M THAP)<sup>a</sup>

complex	half-wave potentials, V vs. SCE				$E_{1/2}^{\text{I-}} / E_{1/2}^{\text{II-}}$
	$E_{1/2}^{\text{I}}$	$E_{1/2}^{\text{II}}$	$E_{1/2}^{\text{III}}$	$E_{1/2}^{\text{IV}}$	
PcZn	-0.86	-1.30	-1.85	-2.25	0.44
$(\text{CN})_8\text{PcZn}$	-0.15 <sup>b</sup>	-0.50	-1.10	-1.35	0.35
TPPZn	-1.32	-1.71	-2.45	-2.67	0.39
$(\text{CN})_4\text{TPPZn}$	-0.36	-0.70	-2.10	-2.25	0.34

<sup>a</sup> Similar values were obtained at a Pt or Au electrode using TBAP as supporting electrolyte. <sup>b</sup> The value presented is for the monomeric form of  $(\text{CN})_8\text{PcZn}$  (labeled 1b in Figure 2). Another wave is observed at  $-0.05$  V (labeled 1a in Figure 2) and is for the aggregated form of  $(\text{CN})_8\text{PcZn}$ .

is generated at  $-0.70$  V vs. SCE. Further electrolysis at a potential corresponding to the third reduction step generates a paramagnetic species ( $g = 2.0050$ ,  $\Delta H = 6$  G), which disappears after generation of the new diamagnetic species at  $-1.50$  V vs. SCE.

Analysis of the initial concentration-dependent absorption spectra, as well as the EPR and electrochemical data, suggests, that the overall four-electron reduction may be described by the following scheme, where 1–4 corresponds to the electrode processes shown in Figure 1:



According to this scheme both aggregated and nonaggregated forms of  $(\text{CN})_8\text{PcZn}$  are present in the bulk of solution,<sup>10</sup> and upon electroreduction, both monomeric and aggregated  $[(\text{CN})_8\text{PcZn}]^{\cdot -}$  are found at the electrode surface. However, no higher charged forms of the aggregate are observed, and it is thus assumed that aggregated  $[(\text{CN})_8\text{PcZn}]^{\cdot -}$  converts to a monomer either before or during the electroreduction at  $-0.50$  V.

Our aim in this electrochemical study of  $(\text{CN})_8\text{PcZn}$  was to reversibly produce stable anion radicals and dianions at potentials more positive than those previously observed for phthalocyanines<sup>11</sup> or the related metalloporphyrins<sup>12</sup> and at the same time to stabilize the reversible formation of both a trianion and a tetraanion by the use of highly electron withdrawing substituents on the phthalocyanine ring. A comparison of the results for the above series of reactions with those for all other nonsubstituted or substituted phthalocyanines<sup>11</sup> shows that both of these goals have been accomplished.

From the potentials in Table I it can be seen that a smaller electron-accepting (substituent) effect from the cyano groups is present for the first two reductions of  $(\text{CN})_8\text{PcZn}$  than for the first two reductions of  $(\text{CN})_4\text{TPPZn}$ . This decrease in substituent effect might be expected for the phthalocyanine derivatives, since the benzene rings only weakly participate in delocalization of the  $\pi$  ligand electrons.<sup>13</sup> At the same time, however, there is the expected substituent effect for the last two reversible reductions of  $(\text{CN})_8\text{PcZn}$ , which does not occur for the last two irreversible reductions of  $(\text{CN})_4\text{TPPZn}$ . This shift of 750 to 900 mV results in an extremely facile third and fourth reduction of the cyano-substituted phthalocyanine derivative, which in the final step yields a stable tetraanion at very low energy ( $E_{1/2} = -1.35$  V vs. SCE).

In conclusion, we have shown that  $(\text{CN})_8\text{PcZn}$  can be reduced by four single-electron-transfer steps to yield mono-, di-, tri-, and

(8) Bannhr, R.; Meyer, G.; Wöhrle, D. *Polym. Bull.*, **1980**, *2*, 841.

(9) Wöhrle, D.; Meyer, G.; Wahl, B. *Makromol. Chem.* **1980**, *181*, 2127.

(10) Aggregation was confirmed at polarographic concentrations of  $(\text{CN})_8\text{PcZn}$  by spectral analysis as a function of phthalocyanine concentration and by the global coulometric value of  $1.0 \pm 0.05$  electrons obtained by controlled-potential electrolysis carried out at potentials between  $-0.2$  and  $-0.4$  V vs. SCE. At concentrations more dilute than  $10^{-6}$  M only monomeric  $(\text{CN})_8\text{PcZn}$  existed in DMF solutions.

(11) Lever, A. B. P.; Licoccia, S.; Magnell, P. C.; Minor, P.; Ramaswami, B. S. *Adv. Chem. Ser.* **1982**, No. 201, 237.

(12) Dolphin, D., Ed. "The Porphyrins"; Academic Press: New York, 1978.

(13) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.

tetraanions at relatively low cathodic potentials. This highly electron accepting compound has redox properties close to the chemical derivatives used to generate charge-transfer complexes such as TCNQ ( $E_{1/2}^I = 0.17$  V;  $E_{1/2}^{II} = -0.37$  V;  $\Delta E = 0.54$  V) or TCNE ( $E_{1/2}^I = 0.15$  V;  $E_{1/2}^{II} = -0.57$  V;  $\Delta E_{1/2} = 0.72$  V)<sup>14</sup> and may allow their use in such complexes.

Studies are presently underway to examine the general chemical reactivity of (CN)<sub>8</sub>PeZn and other similar octacyano-substituted metal phthalocyanine complexes.

**Acknowledgment.** K.M.K. acknowledges the support of the National Science Foundation (Grant CHE-792156).

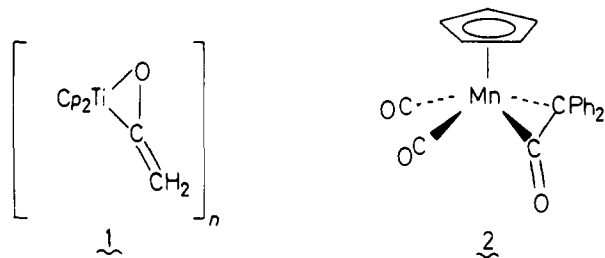
(14) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* 1976, 98, 3916.

## Conversion of an $\eta^5$ -C<sub>5</sub>H<sub>5</sub> Complex into a Cyclopentadienylidene Ketene Complex

Charles P. Casey\* and Joseph M. O'Connor

Department of Chemistry  
University of Wisconsin—Madison  
Madison, Wisconsin 53706  
Received January 10, 1983

Transition-metal ketene complexes have been proposed as intermediates in CO reduction<sup>1</sup> and have been studied as models for CO<sub>2</sub> metal complexes.<sup>2a,b</sup> Two types of metal  $\eta^2$ -ketene complexes are known: early transition metals form  $\eta^2$ -CO complexes<sup>2</sup> such as **1** while later transition metals form  $\eta^2$ -CC com-



plexes such as **2**.<sup>3</sup> Previously, metal ketene complexes have been prepared by direct reaction of ketene with a coordinatively unsaturated metal complex,<sup>2a-d,3a</sup> by carbonylation of metal alkylidene complexes,<sup>3d</sup> and by deprotonation of metal acyl complexes.<sup>2c,4</sup> Here we report that ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(CO)(NO)(CH<sub>3</sub>) (**3**, Scheme I) reacts with high concentrations of PMe<sub>3</sub> to give an  $\eta^1$ -C<sub>5</sub>H<sub>5</sub> derivative, **4**, which is then converted to the novel cyclopentadienylidene ketene<sup>5</sup> complex **5**. This reaction further illustrates the reactivity of the normally unreactive C<sub>5</sub>H<sub>5</sub> ligand.

Previously we have reported that ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Re(CO)(NO)(CH<sub>3</sub>) (**3**) reacts rapidly and reversibly with PMe<sub>3</sub> at room temperature

(1) (a) Blyholder, G.; Emmet, P. H. *J. Phys. Chem.* 1960, 64, 470 and references therein. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* 1980, 13, 121.

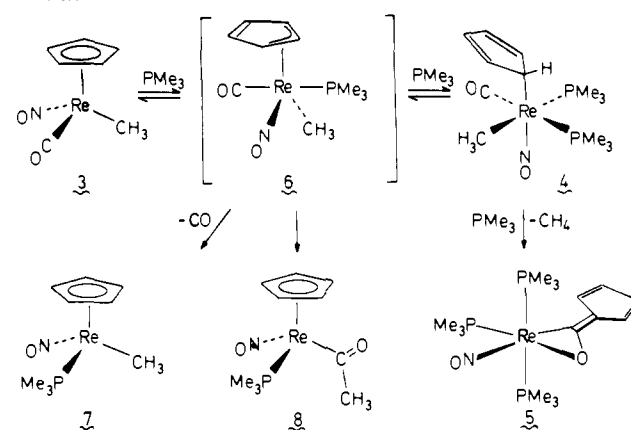
(2) (a) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* 1978, 17, 2995-3002. (b) Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Ibid.* 1981, 20, 1173-1178. (c) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* 1978, 100, 1921-1922. (d) Hoberg, H.; Korff, J. *J. Organomet. Chem.* 1978, 152, 255-264. (e) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* 1982, 104, 5499-5500. (f) Bristow, S. A.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* 1982, 462-464.

(3) (a) Schorpp, K.; Beck, W. *Z. Naturforsch., B* 1973, 28B, 738-740. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1974, 13, 335-336. (c) Redhouse, A. D.; Herrmann, W. A. *Ibid.* 1976, 15, 615-616. (d) Herrmann, W. A.; Plank, J. *Ibid.* 1978, 17, 525-526. (e) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* 1979, 101, 3133-3135.

(4) Lappert<sup>2d</sup> has reported that carbonylation of Cp<sub>2</sub>Zr(CHPh<sub>2</sub>)R gives the  $\eta^2$ -CO complex [Cp<sub>2</sub>Zr(COCPh<sub>2</sub>)<sub>2</sub>]. Grubbs<sup>2e</sup> has suggested that the reaction may proceed by deprotonation of an intermediate Cp<sub>2</sub>Zr(COCHPh<sub>2</sub>)R species.

(5) Cyclopentadienylidene ketene has been observed by IR (2133 (vs), 2130 (s), 1445 (m), 1325 (m) cm<sup>-1</sup>), UV and photoelectron spectroscopy in low-temperature matrices: Torres, M.; Clement, A.; Strausz, O. P. *J. Org. Chem.* 1980, 45, 2273-2274 and references therein.

Scheme I



to give the  $\eta^1$ -C<sub>5</sub>H<sub>5</sub> bisphosphine complex **4** via the proposed  $\eta^3$ -C<sub>5</sub>H<sub>5</sub> monophosphine intermediate **6**. Upon being heated at 90 °C in benzene, the equilibrium mixture of **3** and **4** is slowly converted to a 4:1 mixture of phosphine-substituted methyl and acetyl complexes, **7** and **8**, probably via the same  $\eta^3$ -C<sub>5</sub>H<sub>5</sub> intermediate **6**.<sup>6</sup> We have now discovered that when conversion to **7** and **8** is inhibited by high concentrations of PMe<sub>3</sub>, another reaction leading to cyclopentadienylidene ketene complex **5** takes place.

When a toluene solution of **3** (0.986 mmol, 0.25 M) and PMe<sub>3</sub> (2.9 M) was heated for 17 h at 72 °C,<sup>7</sup> evolution of methane (44%) was detected. Removal of the excess PMe<sub>3</sub> and toluene under reduced pressure and recrystallization of the residue from THF-hexane gave a yellow solid identified as the  $\eta^2$ -CO-cyclopentadienylidene ketene complex **5** (150 mg, 28%).<sup>8</sup>

The <sup>1</sup>H NMR of **5** in benzene-*d*<sub>6</sub> establishes the presence of two equivalent *trans*-PMe<sub>3</sub> ligands ( $\delta$  1.05 (three-line pattern with  $J_{PH} + J_{PH} = 7$  Hz)), one unique PMe<sub>3</sub> ligand ( $\delta$  1.09 (d,  $J = 8.5$  Hz)), and four different coupled protons on the cyclopentadienylidene ketene ligand ( $\delta$  6.89 ( $J = 4.4, 1.8, 1.8$  Hz), 7.03 ( $J = 4.4, 1.6, 1.8$  Hz), 7.20 ( $J = 4.4, 2.4, 1.6$  Hz), 7.30 ( $J = 4.4, 2.4, 1.8$  Hz)).<sup>9</sup> The observation of four different protons on the five-membered ring excludes a more symmetric  $\eta^2$ -CC-cyclopentadienylidene ketene complex for which only two different resonances would be possible.

The IR spectrum of **5** (Nujol) has a band at 1602 cm<sup>-1</sup> assigned to a linear nitrosyl ligand. A broad band at 1555 cm<sup>-1</sup> might be due to either the C-O or C=C stretch of the  $\eta^2$ -CO-cyclopentadienylidene ketene ligand. For comparison, the  $\eta^2$ -CO-complex **1** has a band at 1610 cm<sup>-1</sup><sup>2e</sup> while the  $\eta^2$ -CC-complex **2** has a band at 1787 cm<sup>-1</sup>.<sup>3b</sup>

In the <sup>13</sup>C{<sup>1</sup>H} NMR of **5** in CD<sub>2</sub>Cl<sub>2</sub>, the ketene carbon bonded to rhenium appears as a broad signal at  $\delta$  214.4<sup>10</sup> with  $\nu_{1/2} = 29$  Hz. The relatively narrow line width of this signal is consistent

(6) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* 1980, 102, 6154-6156. Casey, C. P.; Jones, W. D.; Harsy, S. G. *J. Organomet. Chem.* 1981, 206, C38-C42. Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics*, in press.

(7) The <sup>1</sup>H NMR of a similar benzene-*d*<sub>6</sub> solution at 72 °C shows that the  $\eta^1$ -C<sub>5</sub>H<sub>5</sub> complex **4** is the major species under these initial conditions.

(8) <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.09 M Cr(acac)<sub>3</sub>)  $\delta$  214.1 ( $\nu_{1/2} = 29$  Hz), 125.0 (d,  $J_{CH} = 162$  Hz), 120.3, 119.0 (d,  $J_{CH} = 156$  Hz), 118.0 (d,  $J_{CH} = 159$  Hz), 112.3 (d,  $J_{CH} = 165$  Hz), 16.16 (q, t,  $J_{CH} = 127$  Hz,  $J_{PC} + J_{PC} = 27.9$  Hz), 21.1 (q, d,  $J_{CH} = 127$  Hz,  $J_{PC} = 27.8$  Hz); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  -26.6 (d,  $J_{PP} = 7.9$  Hz), -32.9 (t,  $J_{PP} = 7.9$  Hz) relative to external H<sub>3</sub>PO<sub>4</sub>. Anal. Calcd for C<sub>15</sub>H<sub>31</sub>NO<sub>2</sub>P<sub>3</sub>Re: C, 33.59; H, 5.83; N, 2.61. Found: C, 33.63; H, 5.83; N, 2.80. *m/e* calcd for C<sub>15</sub>H<sub>31</sub>NO<sub>2</sub>P<sub>3</sub>Re, 537.1121; obsd 537.1130. Molecular weight by osmometry in dichloroethane 502, calcd 536.

(9) The magnitudes of these coupling constants are similar to those observed for fulvene derivatives: Hollenstein, R.; von Philipsborn, W.; Vögeli, R.; Neuenchwander, M. *Helv. Chim. Acta* 1973, 56, 847-859.

(10) For comparison, the ketene carbon bonded to oxygen in **1** comes at  $\delta$  220<sup>2e</sup> and for **2** at  $\delta$  201.3.<sup>3b</sup> Additional resonances of **5** were observed for the carbons of the five-membered ring at  $\delta$  125.0, 120.3, 119.0, 118.0, and 112.3; for the unique PMe<sub>3</sub> ligand at  $\delta$  21.1 (d,  $J_{PC} = 27.8$  Hz) and for the equivalent *trans* PMe<sub>3</sub> ligands at  $\delta$  16.2 (three-line pattern with  $J_{PC} + J_{PC} = 27.9$  Hz).