

in the reaction of  $T_{OH}^0$  because this negative charge is (partially) compensated by the positive charge on water (2) or by protonation (3).

Another factor which could reduce the imbalance in the transition state of the water-catalyzed reaction is that in general a very late transition state is less likely to be strongly imbalanced. This is best visualized if one places the reaction coordinate on a diagram with separate axes for C-C bond cleavage and for charge delocalization. As the reaction coordinate approaches the product corner, it inevitably also approaches the diagonal line for balanced reactions. If the larger secondary isotope effects for the water reaction (1.24 to 1.28) compared to that of the  $k_4$  step (1.20) is a true indication of a later transition state, this factor could be significant.

**C. Water Addition to the Double Bond,  $K_1$ .** We note that the equilibrium isotope effect on  $K_1$  (average  $K_1^H/K_1^D = 0.906$ ) is substantially smaller than the equilibrium isotope effects for nucleophilic addition to carbonyl carbon.<sup>36,57,58</sup> Whether this is typical for the addition to activated olefins will have to await further study. Nevertheless, it is noteworthy that this result is consistent with expectations based on fractionation factor calculations.<sup>65</sup>

### Experimental Section

**Materials.** 1-H, 1-NO<sub>2</sub>, and 1-OMe were available from a previous study.<sup>1</sup> The deuterated analogues were synthesized by condensation of Meldrum's acid with the respective deuterated benzaldehyde as described by Schuster et al.,<sup>66</sup> the isotopic purity of the deuterated olefins was 98% or better as shown by NMR analysis. Benzaldehyde-*d*<sub>1</sub> was prepared by the method of Schowen et al.,<sup>67</sup> *p*-methoxybenzaldehyde-*d*<sub>1</sub> by the me-

thod of Vitullo et al.,<sup>68</sup> *p*-nitrobenzaldehyde-*d*<sub>1</sub> by a modification<sup>21</sup> of Kirby's<sup>69</sup> procedure.

Morpholine and triethylamine were purified by refluxing for 8 h over sodium followed by distillation under nitrogen. The other materials were all reagent grade and were used without further purification.

**Equilibrium Measurements.**  $K_1^H$  and  $K_1^D$  were measured spectrophotometrically at  $\lambda_{max}$  of the olefin (325 nm for 1-H, 320 nm for 1-NO<sub>2</sub>, 372 nm for 1-OMe); at these wavelengths  $T_{OH}^-$  does not absorb.  $pK_1$  was obtained as

$$pK_1 = pH + \log \frac{OD}{OD_0 - OD} \quad (21)$$

where OD refers to the optical density at a pH close to  $pK_1$  while  $OD_0$  is the optical density of a solution where all the material is in the olefin form. Since the solutions were unstable owing to the onset of the hydrolysis reaction, the following procedure was adopted. A few microliters of a stock solution of the olefin in Me<sub>2</sub>SO as injected into a prethermostated buffer solution placed into a cuvette of a Gilford spectrophotometer. The OD was recorded as a function of time with the time of injection being  $t = 0$ . Logarithmic plots of  $\Delta OD$  vs. time were extrapolated to  $t = 0$  in order to obtain the desired OD.

**Kinetic Experiments.** The techniques used were the same as the ones reported before.<sup>1,3</sup>

**Acknowledgment.** This research was supported by Grant CHE80-24261 from the National Science Foundation. We wish to thank Professor William P. Jencks for criticisms and suggestions.

**Registry No.** 1-H, 1214-54-6; 1-NO<sub>2</sub>, 15795-62-7; 1-OMe, 15795-54-7.

**Supplementary Material Available:** Tables S1-S4, observed rate constants for hydrolytic cleavage of 1-NO<sub>2</sub> and 1d-NO<sub>2</sub> (S1), of 1-H and 1d-H (S2), and of 1-OMe and 1d-OMe (S3); observed rate constants for hydrolytic cleavage of 1-NO<sub>2</sub>, 1-H, and 1-OMe, additional data (S4); synthesis of *p*-nitrobenzaldehyde-*d*<sub>1</sub> (9 pages). Ordering information is given on any current masthead page.

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## Reactivity of Some Transition-Metal Systems toward Liquid Carbon Dioxide

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**Abstract:** The reactivity of several transition-metal complexes toward liquid CO<sub>2</sub> has been investigated as a means of screening such complexes for their ability to bind CO<sub>2</sub>. Although the known Ni(CO<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> complex was prepared by the reaction of [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>( $\mu$ -N<sub>2</sub>) with CO<sub>2</sub>(l), the compounds Pd(PCy<sub>3</sub>)<sub>2</sub> and Pt(PCy<sub>3</sub>)<sub>2</sub> do not react with CO<sub>2</sub>(l) to afford CO<sub>2</sub> complexes. But the compound Pt(PCy<sub>3</sub>)<sub>2</sub> does react with wet CO<sub>2</sub> to afford PtH(O<sub>2</sub>COH)(PCy<sub>3</sub>)<sub>2</sub>, a bicarbonato complex. Similar reactivity was seen for W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>, which produces WH(O<sub>2</sub>COH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> in wet CO<sub>2</sub>(l). The compounds Na[Co(N<sub>2</sub>)(PEt<sub>2</sub>Ph)<sub>3</sub>] and [Co(PEt<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub>( $\mu$ -N<sub>2</sub>) react with CO<sub>2</sub>(l) to form complexes that contain carbonyl and carbonato ligands. Peroxocarbonato complexes, IrR(OCO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (R = Me, Ph), were prepared from IrR(O<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> with CO<sub>2</sub>(l).

Carbon dioxide offers an attractive potential alternative to carbon monoxide in the development of a C<sub>1</sub> chemical technology to supplement present petroleum-based technology. Before such a development can be realized, transition-metal-carbon dioxide interactions must be studied, as it is presumed that the catalytic reduction of carbon dioxide, if it is to be accomplished at all, will be carried out in the presence of a transition metal.<sup>1</sup>

Eisenberg and Hendriksen<sup>1</sup> recently reviewed the coordination chemistry of carbon dioxide and summarized some examples of metal complexes originally believed to be those of carbon dioxide that on further examination turned out to be otherwise. Because of difficulties of spectroscopic characterization, the unpredictable effects of adventitious water, and the tendency of coordinated CO<sub>2</sub> to react further, it is prudent to accept structural characterization by diffraction methods as the criterion for judging the authenticity of a given class of transition-metal-carbon dioxide complexes

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(M-CO<sub>2</sub>). To our knowledge only three M-CO<sub>2</sub> complexes, Ni( $\eta^2$ -CO<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>,<sup>2,3</sup> K[Co(Pr-salen)( $\eta^1$ -CO<sub>2</sub>)],<sup>4</sup> and Nb( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)( $\eta^2$ -CO<sub>2</sub>),<sup>5</sup> have been so characterized, despite the intense effort that has been devoted to the preparation of such complexes. The Ni complex appears to have the correct balance of electronic and steric factors for the stabilization of bound CO<sub>2</sub>, as the complexes M( $\eta^2$ -CO<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub> (M = Pd, Pt; R = Cy (vide infra), Ph<sup>6</sup>) cannot be prepared. The stability of the Nb complex has been ascribed to its coordinative saturation and to the fact that the orientation of the bound CO<sub>2</sub> ligand disfavors an internal decomposition route. The stability of the Co complex has been ascribed to the simultaneous involvement of the Lewis acid site at C with Co and of the Lewis base site at O with K.

The existence of these three M-CO<sub>2</sub> complexes provides meager clues as to how one might develop a general coordination chemistry of CO<sub>2</sub>. What is needed at this stage is a convenient method for surveying the reactivity of CO<sub>2</sub> toward a wide spectrum of transition-metal complexes. While previous studies have used gaseous CO<sub>2</sub>, we describe here some experiments on the reactivity at room temperature of a number of transition-metal complexes toward liquid CO<sub>2</sub>. We believe that the benefits of using liquid CO<sub>2</sub> are a greatly increased CO<sub>2</sub> concentration and the elimination of solvent competition for a vacant coordination site on the metal. Therefore, the use of liquid CO<sub>2</sub> may be an effective way to survey metal complexes for their ability to bind CO<sub>2</sub>.

In this initial study, each of the metal systems chosen generally has the following characteristics: a low-valent metal atom is surrounded by electron-donating ligands, usually trialkylphosphine ligands; the compound is either coordinatively unsaturated or contains an easily displaceable ligand such as N<sub>2</sub> or an olefin; and at least some of the ligands about the metal are sterically demanding.

## Experimental Section

All reactions were performed under an atmosphere of prepurified N<sub>2</sub> with standard Schlenkware. Air-sensitive solids were handled in a Vacuum Atmosphere glove box under an Ar atmosphere. Solvents were refluxed under N<sub>2</sub> over Na/benzophenone and were distilled immediately prior to use. The compounds PPh<sub>3</sub>, PEt<sub>2</sub>Ph, and Cy<sub>3</sub>PCS<sub>2</sub> were purchased from Strem Chemicals, Inc. The compound PCy<sub>3</sub> was generated by dissolving Cy<sub>3</sub>PCS<sub>2</sub> in ethanol and distilling CS<sub>2</sub> from it. All other organic reagents were purchased from Aldrich Chemical Co. The compounds IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>,<sup>7</sup> IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>,<sup>8</sup> Ir(CH<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>,<sup>9</sup> Ir(C<sub>6</sub>H<sub>5</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>,<sup>10</sup> [RhH(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>( $\mu$ -N<sub>2</sub>),<sup>11</sup> W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>,<sup>12</sup> Mo(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>,<sup>12</sup> [Co(PEt<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub>( $\mu$ -N<sub>2</sub>),<sup>13</sup> [Co(PPh<sub>3</sub>)<sub>3</sub>]<sub>2</sub>( $\mu$ -N<sub>2</sub>),<sup>13</sup> Na[Co(N<sub>2</sub>)(PEt<sub>2</sub>Ph)]<sub>3</sub>,<sup>13</sup> [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>( $\mu$ -N<sub>2</sub>),<sup>14</sup> Pd(PCy<sub>3</sub>)<sub>2</sub>,<sup>15</sup> and Pt(PCy<sub>3</sub>)<sub>2</sub><sup>15</sup> were prepared as described in the literature. Coleman Instrument Grade CO<sub>2</sub> was obtained from Matheson and dried by passage through a 2 × 40 cm column of activated 3-Å molecular sieves (Davison).

(2) Abbreviations used: Cy = cyclohexyl, Pr-salen = *o*-HOC<sub>6</sub>H<sub>4</sub>C(Pr)=N(CH<sub>2</sub>)<sub>2</sub>N=C(Pr)C<sub>6</sub>H<sub>4</sub>OH-*o*, Ph = phenyl, Et = ethyl, Me = methyl.

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Table I. Reactivity of Some Transition-Metal Systems toward Liquid CO<sub>2</sub>

complex	reacts with dry CO <sub>2</sub>	reacts with wet CO <sub>2</sub>
IrCl(N <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	no	
IrR(CO)(PPh <sub>3</sub> ) <sub>2</sub> , R = Me, Ph	no	
IrR(O <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> , R = Me, Ph	yes	
[RhH(PCy <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ( $\mu$ -N <sub>2</sub> )	no	
[Ni(PCy <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ( $\mu$ -N <sub>2</sub> )	yes	
Pd(PCy <sub>3</sub> ) <sub>2</sub>	no	
Pt(PCy <sub>3</sub> ) <sub>2</sub>	no	yes
Mo(CO) <sub>3</sub> (PCy <sub>3</sub> ) <sub>2</sub>	no	
W(CO) <sub>3</sub> (PCy <sub>3</sub> ) <sub>2</sub>	no	yes
[Co(PPh <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> ( $\mu$ -N <sub>2</sub> )	no	
[Co(PEt <sub>2</sub> Ph) <sub>3</sub> ] <sub>2</sub> ( $\mu$ -N <sub>2</sub> )	yes	
Na[Co(N <sub>2</sub> )(PEt <sub>2</sub> Ph)] <sub>3</sub>	yes	

A Perkin-Elmer 283 spectrometer was used to record IR spectra. The NMR spectra were obtained from a JEOL FX90Q spectrometer on samples in 10-mm tubes. <sup>1</sup>H spectra are referenced to external Me<sub>4</sub>Si and the <sup>31</sup>P{<sup>1</sup>H} NMR spectra to external 85% H<sub>3</sub>PO<sub>4</sub> with positive chemical shift values to lower field.

A Parr Instruments, Inc., 45-mL pressure vessel was used for the liquid CO<sub>2</sub> experiments. A typical run consisted of placing 0.1-0.15 g of starting metal complex and a stirring bar into the quartz-lined pressure vessel under an inert atmosphere. A measured amount of CO<sub>2</sub>(g) ( $\approx$  3500 cm<sup>3</sup>, enough to yield  $\sim$ 10 mL CO<sub>2</sub>(l)) was condensed into the vessel cooled by a dry ice/ether bath ( $-100$  °C). This corresponds roughly to about a 1000-fold molar excess of CO<sub>2</sub> to metal complex. The system was then sealed, placed behind a blast shield, and brought to room temperature (pressure in vessel 60-70 atm). Since the critical temperature of CO<sub>2</sub> is 31 °C and the pressure limit in the vessel is  $\approx$ 120 atm, experiments at elevated temperatures were not carried out. The reaction mixture was stirred for 1 h to 2 weeks, depending on the compound under study. The CO<sub>2</sub> was then vented, the pressure vessel opened under an inert atmosphere, and the nature of the metal complex probed spectroscopically. The presence of trace amounts of H<sub>2</sub>O in CO<sub>2</sub> must be considered when one evaluates the nature of the products obtained, whether with gaseous or liquid CO<sub>2</sub>. Therefore, if on the basis of spectroscopic examination of the products a reaction was judged to have occurred, the experiment was repeated with water deliberately added to the reaction mixture. If the yield of the same product increased, then the reaction was assumed to require wet CO<sub>2</sub>; if the yield of product did not change, the reaction was assumed to occur with dry CO<sub>2</sub>.

## Results

We divide our findings on the reactivity at room temperature of transition-metal complexes toward liquid CO<sub>2</sub> into three categories: no reaction; reaction with dry CO<sub>2</sub>; and reaction with wet CO<sub>2</sub>. The various reactivities are summarized in Table I.

**No Reaction.** As Table I indicates, a number of the complexes studied show no reactivity toward liquid CO<sub>2</sub>. These compounds were recovered unchanged from the reaction vessel, although the fact that they were generally dispersed over the quartz liner argues for their having been dissolved in liquid CO<sub>2</sub>. Although the experimental conditions did not enable us to observe or probe the reaction mixtures under pressure, at least for the N<sub>2</sub>-containing complexes of Table I, the persistence of N<sub>2</sub> as a ligand argues against CO<sub>2</sub> reactivity at high pressure. Thus, CO<sub>2</sub> did not displace N<sub>2</sub> from IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>. There is no evidence that CO<sub>2</sub> will insert into the Ir-R bond of IrR(CO)(PPh<sub>3</sub>)<sub>2</sub>, R = Me, Ph. Moreover, in a separate experiment, the addition of CH<sub>3</sub>I to IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> in liquid CO<sub>2</sub> proceeded smoothly to afford IrClI(CH<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, as judged by comparison of the spectral properties of an authentic sample prepared in toluene. Thus, there is no evidence of CO<sub>2</sub> insertion into the Ir-CH<sub>3</sub> bond.

Speier et al.<sup>16</sup> report that Co(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub> reacts with CO<sub>2</sub> in toluene to produce [Co(CO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sub>n</sub>. However, we find that [Co(PPh<sub>3</sub>)<sub>3</sub>]<sub>2</sub>( $\mu$ -N<sub>2</sub>) shows no reactivity toward CO<sub>2</sub>, although the corresponding PEt<sub>2</sub>Ph complex does. The results for the Ph complexes may not be at variance, for it seems doubtful if a CO<sub>2</sub>

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complex was prepared by Speier et al.<sup>16</sup> They assign to the coordinated CO<sub>2</sub> molecule an IR vibration at 1890 cm<sup>-1</sup>. This is well beyond the range of 1550–1740 cm<sup>-1</sup> observed in authentic CO<sub>2</sub> complexes.<sup>1</sup>

Although [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>) is known to react with CO<sub>2</sub>(g) to afford Ni(η<sup>2</sup>-CO<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>,<sup>3</sup> and indeed this same complex is formed with CO<sub>2</sub>(l) (vide infra), the closely related complexes Pd(PCy<sub>3</sub>)<sub>2</sub> and Pt(PCy<sub>3</sub>)<sub>2</sub> do not react with dry CO<sub>2</sub>, although the Pt compound does react with wet CO<sub>2</sub>. Nor does the related Rh system, [RhH(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>), display any reactivity toward CO<sub>2</sub>. Finally, the earlier transition-metal systems, M(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>, M = Mo, W,<sup>12</sup> do not react with dry CO<sub>2</sub>, although the W complex does react with wet CO<sub>2</sub>.

**Reactions with Dry CO<sub>2</sub>.** The compound Ir(CH<sub>3</sub>)(O<sub>2</sub>)-(CO)(PPh<sub>3</sub>)<sub>2</sub>, prepared by exposing Ir(CH<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> to the atmosphere for 24 h, shows reactivity toward dry CO<sub>2</sub>(l). The oxygen complex shows a ν<sub>CO</sub> band at 1968 cm<sup>-1</sup> and a ν<sub>OO</sub> band at 826 cm<sup>-1</sup>. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum consists of a singlet at -2.56 ppm. The <sup>1</sup>H NMR spectrum displays a triplet resonance at 0.40 ppm (*J*<sub>PH</sub> = 4.9 Hz). The product of the reaction with dry CO<sub>2</sub> shows a ν<sub>CO</sub> band at 2015 cm<sup>-1</sup> and absorption bands at 1680 and 772 cm<sup>-1</sup>. Its <sup>31</sup>P{<sup>1</sup>H} NMR spectrum consists of a singlet at 8.58 ppm. Its <sup>1</sup>H NMR spectrum displays a triplet resonance at 0.51 ppm (*J*<sub>PH</sub> = 4.9 Hz). The compound Pt(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> reacts with CO<sub>2</sub> to afford Pt(OCO<sub>3</sub>)(PCy<sub>3</sub>)<sub>2</sub>,<sup>17</sup> which displays vibrations at 1680 and 822 cm<sup>-1</sup> that have been assigned to the C=O and O—O stretching vibrations of the peroxy-carbonato ligand. The close correspondence of the vibrational spectra of the Ir and Pt systems, along with the NMR evidence on the Ir system, leads us to suggest that the complex formed between Ir(CH<sub>3</sub>)(O<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> and CO<sub>2</sub>(l) is Ir(CH<sub>3</sub>)-(OCO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, in which the phosphines are trans to one another. Comparisons of the spectra suggest similarly that the product of Ir(C<sub>6</sub>H<sub>5</sub>)(O<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> with CO<sub>2</sub>(l) is also a peroxy-carbonate.

The ready displacement of the N<sub>2</sub> ligand from [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>) led us to examine other first-row transition-metal dinitrogen complexes. The compound [Co(PET<sub>2</sub>Ph)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>) reacts with liquid CO<sub>2</sub> to yield a highly air-sensitive red oil. The reaction is accompanied by the release of PET<sub>2</sub>Ph. The IR spectrum of the product displays intense bands at 1910, 1855, and 1715 cm<sup>-1</sup> and no evidence of OPET<sub>2</sub>Ph formation. The red compound is paramagnetic, making NMR spectral measurements impossible. Exposure of the product to air converts it into a very insoluble purple solid containing Co(CO)<sub>3</sub>, as judged by comparison of the IR spectrum with that of an authentic sample of Co(CO)<sub>3</sub> prepared from Co(ClO<sub>4</sub>)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>. The infrared bands at 1910 and 1855 cm<sup>-1</sup> might arise from carbonyl vibrations, and the band at 1715 cm<sup>-1</sup> could be assigned to a metal-carbonato vibration (compare the 1680 cm<sup>-1</sup> band in Pt(CO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>).<sup>18</sup> The reductive disproportionation of CO<sub>2</sub> to CO and CO<sub>3</sub><sup>2-</sup> has been observed previously in [Mo(CO<sub>3</sub>)(CO)(PMe<sub>2</sub>Ph)<sub>2</sub>]<sub>2</sub>,<sup>19</sup> [Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>(CO)<sub>2</sub>,<sup>20</sup> and the reaction of Na[Fe(C<sub>5</sub>H<sub>5</sub>)(CO)]<sub>2</sub> with CO<sub>2</sub>.<sup>21</sup> The intermediacy of a C<sub>2</sub>O<sub>4</sub> ligand, as observed in IrCl(C<sub>2</sub>O<sub>4</sub>)(PMe<sub>3</sub>)<sub>2</sub>,<sup>22</sup> is an attractive idea but has not been conclusively demonstrated for any system to date.

Similar chemistry was seen for Na[Co(N<sub>2</sub>)(PET<sub>2</sub>Ph)<sub>3</sub>] in liquid CO<sub>2</sub>. The starting metal complex displays a NN stretching frequency at 1840 cm<sup>-1</sup>. This is absent in the reaction product, and new bands are present at 1974, 1910, and 1715 cm<sup>-1</sup>. These can again be assigned to metal-carbonyl and metal-carbonate vibrations. No OPET<sub>2</sub>Ph was detected, and the compound again

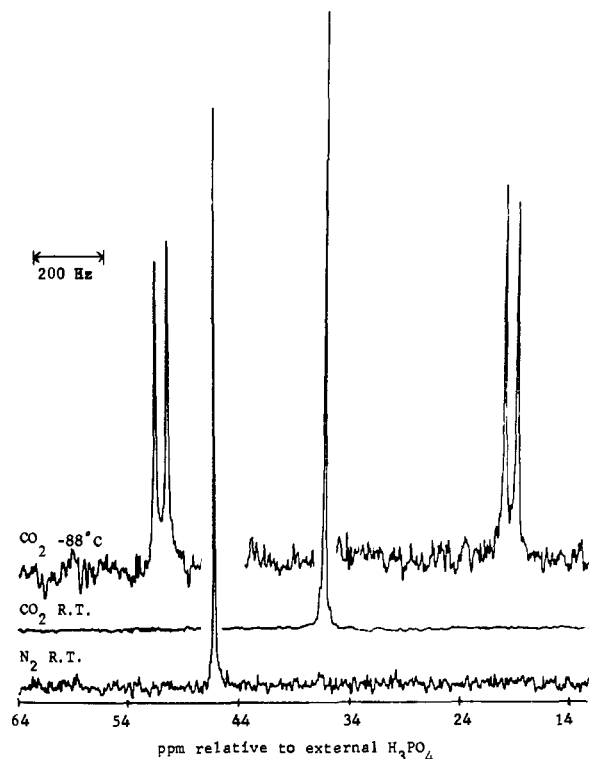
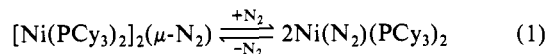


Figure 1. <sup>31</sup>P{<sup>1</sup>H} NMR spectral changes observed upon adding CO<sub>2</sub> to a toluene-*d*<sup>8</sup> solution of Ni(N<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> and then cooling the Ni(CO<sub>2</sub>)-(PCy<sub>3</sub>)<sub>2</sub> solution that is formed.

decomposed in air to a purple solid containing Co(CO)<sub>3</sub>.

The reaction of [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>) with CO<sub>2</sub>(g) was first reported to afford [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-CO<sub>2</sub>).<sup>14</sup> Later, Ni(η<sup>2</sup>-CO<sub>2</sub>)-(PCy<sub>3</sub>)<sub>2</sub> was isolated from this reaction, as characterized by a single-crystal X-ray diffraction study.<sup>3</sup> We find that this complex may be prepared in high yield in liquid CO<sub>2</sub>. In N<sub>2</sub>-saturated toluene solution, the equilibrium



is confirmed from the observation of an N—N stretching vibration.<sup>14</sup> This vibration is absent in the solid-state IR spectrum, as expected for a symmetrical dimer. We have studied this equilibrium with the use of <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>) in toluene-*d*<sup>8</sup> solution at 30 °C consists of a singlet at 46.5 ppm that is assignable to Ni(N<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>. If argon is bubbled through the solution, N<sub>2</sub> is displaced, and a signal arising from Ni(PCy<sub>3</sub>)<sub>2</sub> is observed at 44.2 ppm. When an N<sub>2</sub>-saturated solution of Ni(N<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> is cooled, the resonance assigned to [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>) appears at 7.35 ppm. Even at -88 °C the equilibrium is not completely shifted to the left, and observable amounts of Ni(N<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> persist. There is a spectral change when CO<sub>2</sub> is bubbled through a solution of [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>) (Figure 1). The resonance arising from the starting material disappears, and a signal assigned to Ni(CO<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> is observed. At 30 °C the spectrum consists of a singlet at 36.16 ppm, but upon cooling the sample the signal coalesces at -50 °C and then sharpens into the expected doublet-of-doublets pattern for two mutually coupled inequivalent cis phosphine ligands (51.5, 20.0 ppm; *J*<sub>PP</sub> = 40.3 Hz). The Δ*G*<sub>c</sub><sup>‡</sup> for this exchange process is 9.8 ± 0.2 kcal/mol.<sup>23</sup>

**Reactions with Wet CO<sub>2</sub>.** The presence of adventitious water has resulted in the misformulations of several "CO<sub>2</sub>" compounds.<sup>24–28</sup> Consequently, as we indicated above, if a given

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transition-metal complex appeared to react with dry CO<sub>2</sub>(l), we repeated the experiment with water deliberately added to the reaction mixture (M:H<sub>2</sub>O = 1:1) to ascertain if the reaction was really occurring not with dry CO<sub>2</sub> but with wet CO<sub>2</sub>. As Table I indicates, we have found that both Pt(PCy<sub>3</sub>)<sub>2</sub> and W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> react with wet CO<sub>2</sub>.

The compound Pt(PCy<sub>3</sub>)<sub>2</sub>, which is known to react with H<sub>2</sub>O,<sup>29</sup> reacts with wet CO<sub>2</sub> to produce *trans*-PtH(O<sub>2</sub>COH)(PCy<sub>3</sub>)<sub>2</sub>. This formulation is based on IR, <sup>1</sup>H NMR, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The IR spectrum displays a Pt-H stretching vibration at 2240 cm<sup>-1</sup>, together with a CO vibration at 1609 cm<sup>-1</sup> and an OH vibration at 2660 cm<sup>-1</sup> that may be assigned to the bicarbonato ligand. The <sup>1</sup>H NMR spectrum displays a signal at -23.59 ppm (*J*<sub>PH</sub> = 14.2 Hz, *J*<sub>PHH</sub> = 1178 Hz) assignable as the hydride resonance and a broad peak at 11.78 ppm attributable to the bicarbonato proton. The *trans* arrangement of the phosphine ligands is confirmed by the observation of a singlet at 39.91 ppm accompanied by <sup>195</sup>Pt satellites (*J*<sub>PTP</sub> = 2920 Hz) in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. Two closely related compounds, *trans*-PtH(η<sup>1</sup>-O<sub>2</sub>COCH<sub>3</sub>)(PCy<sub>3</sub>)<sub>2</sub><sup>30</sup> and *trans*-Pd(CH<sub>3</sub>)(η<sup>1</sup>-O<sub>2</sub>COH)(PEt<sub>3</sub>)<sub>2</sub>,<sup>27</sup> are known.

We find that W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> reacts both with H<sub>2</sub>O and with CO<sub>2</sub>/H<sub>2</sub>O mixtures. The product with H<sub>2</sub>O is highly labile and reverts to W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> in a dry atmosphere or in vacuo. Since the compound is insoluble in hydrocarbon solvents and reacts with donor or chlorinated solvents, no NMR spectral measurements were possible. Its IR spectrum consists of two peaks in the ν<sub>OH</sub> region at 3635 and 3662 cm<sup>-1</sup> and a series of bands at 1925, 1862, 1800, 1709, and 1678 cm<sup>-1</sup>. Treatment of W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> with D<sub>2</sub>O produces the deuterated analogue. Its IR spectrum lacks the bands at 3635, 3662, 1709, and 1678 cm<sup>-1</sup> and displays new vibrations at 2718, 2698, 1696, and 1242 cm<sup>-1</sup>. The question arises whether the complex is better formulated as W(H<sub>2</sub>O)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> or as WH(OH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>. The IR vibrations expected for a metal-coordinated H<sub>2</sub>O<sup>31</sup> are a stretching mode below 3500 cm<sup>-1</sup> and a bending mode near 1600 cm<sup>-1</sup>, both of weak intensity. For a hydrido-hydroxo complex, a M-OH stretching vibration above 3500 cm<sup>-1</sup><sup>31</sup> and a M-H stretching mode should be observed. Thus, we believe the compound is WH(OH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>. The two peaks in the ν<sub>OH</sub> region probably arise from intermolecular interactions; two peaks are also seen for Pt(CH<sub>3</sub>)(OH)(PPh<sub>3</sub>)<sub>2</sub><sup>32</sup> and Pd(OH)(CCl<sub>2</sub>Cl<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>.<sup>32</sup> Deuteration again produces two bands in the ν<sub>OD</sub> region at 2718 and 2698 cm<sup>-1</sup> (ν<sub>OH</sub>/ν<sub>OD</sub> = 1.35). Assignment of the ν<sub>H</sub> vibration can be made on the basis of a ν<sub>D</sub> band at 1242 cm<sup>-1</sup>, assuming ν<sub>H</sub>/ν<sub>D</sub> ~ 1.4. The W-H vibration is then expected to be at ~1700 cm<sup>-1</sup>. The hydride complex displays two bands in this region (1709, 1678 cm<sup>-1</sup>). The compound WH(OH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> is a member of a small class of hydrido-hydroxo complexes formed by oxidative addition of H<sub>2</sub>O. The compounds PtH(OH)(P(*i*-Pr)<sub>3</sub>)<sub>2</sub>,<sup>29</sup> [RhH(OH)(en)<sub>2</sub>]<sup>+</sup>,<sup>33</sup> and Os<sub>3</sub>H(OH)(CO)<sub>10</sub><sup>34</sup> have been reported. Addition of NaOH to RuHCl(PPh<sub>3</sub>)<sub>2</sub> produces RuH(OH)(S)(PPh<sub>3</sub>)<sub>2</sub><sup>35</sup> (S = solvent). The reaction of Pt(PR<sub>3</sub>)<sub>3</sub> (R = *i*-Pr, Et) with H<sub>2</sub>O affords [PtH(PR<sub>3</sub>)<sub>3</sub>][OH] and [PtH(S)-

(PR<sub>3</sub>)<sub>2</sub>][OH].<sup>29</sup> Likewise, RhH(P(*i*-Pr)<sub>3</sub>)<sub>3</sub> oxidatively adds H<sub>2</sub>O to afford [RhH<sub>2</sub>(S)<sub>2</sub>(P(*i*-Pr)<sub>3</sub>)<sub>2</sub>][OH],<sup>36</sup> which can be isolated as the BPh<sub>4</sub><sup>-</sup> salt.

Reaction of WH(OH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> in liquid CO<sub>2</sub> produces WH(O<sub>2</sub>COH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>, a labile bicarbonato complex, which in vacuo reverts to W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>. The formulation as WH(O<sub>2</sub>COH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> is made on the basis of the disappearance of the ν<sub>OH</sub> and ν<sub>H</sub> vibrations and the appearance of a new ν<sub>H</sub> vibration of 2010 cm<sup>-1</sup> and a ν<sub>O<sub>2</sub>COH</sub> vibration at 1615 cm<sup>-1</sup>. Deuteration shifts these frequencies to 1380 and 1605 cm<sup>-1</sup>, respectively. In both complexes there are bands at 1894, 1860, and 1795 cm<sup>-1</sup> in the CO stretching region. The OH stretching vibration could not be located for the bicarbonato ligand. These absorptions are usually broad and weak if there is any intermolecular hydrogen bonding.<sup>28</sup> There is no sign of insertion into the W-H bond. Other cases are known<sup>28</sup> in which insertion into M-OH bonds occurs preferentially over insertion into M-H bonds.

## Discussion

Even under the forcing conditions of liquid CO<sub>2</sub>, with no solvent present and a CO<sub>2</sub>:M ratio of perhaps 1000:1, most metal complexes examined remained unreactive toward CO<sub>2</sub>. But in the course of this survey of the reactivity of some transition-metal systems toward CO<sub>2</sub>(l), several interesting reactions were found, as deduced from the nature of the products.

The formation of IrR(OCO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> from IrR(O<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> is probably an example of external attack by CO<sub>2</sub> on a coordinated species. The compounds IrR(O<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> are coordinately saturated, and even if an open coordination site were provided by PPh<sub>3</sub> dissociation, CO<sub>2</sub> coordination to the iridium atom would seem unlikely because of the demonstrated inertness of IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> and IrR(CO)(PPh<sub>3</sub>)<sub>2</sub> to CO<sub>2</sub>. Kinetic measurements for the reaction of hexafluoroacetone with IrCl(O<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub><sup>37</sup> to form IrCl(O<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>O)(CO)(PPh<sub>3</sub>)<sub>2</sub> are consistent with a similar external attack mechanism for this reaction.

Similarly, the formation of WH(O<sub>2</sub>COH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> from WH(OH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> and CO<sub>2</sub>(l) probably results from external attack of the CO<sub>2</sub> molecule on the W-OH linkage, as it seems unlikely that prior to insertion CO<sub>2</sub> could coordinate to a seven-coordinate W atom. But the formation of *trans*-PtH(O<sub>2</sub>COH)(PCy<sub>3</sub>)<sub>2</sub> from the reaction of Pt(PCy<sub>3</sub>)<sub>2</sub> with wet CO<sub>2</sub>(l) could proceed through CO<sub>2</sub> attack on a *trans*-PtH(OH)(PCy<sub>3</sub>)<sub>2</sub> intermediate, formed by oxidative addition of H<sub>2</sub>O to Pt(PCy<sub>3</sub>)<sub>2</sub>, or by oxidative addition of H<sub>2</sub>CO<sub>3</sub> to Pt(PCy<sub>3</sub>)<sub>2</sub>.

Spectroscopic evidence for CO and CO<sub>3</sub><sup>2-</sup> in the products of the reactions of [Co(PEt<sub>2</sub>Ph)<sub>3</sub>](μ-N<sub>2</sub>) and Na[Co(N<sub>2</sub>)(PEt<sub>2</sub>Ph)<sub>3</sub>] with CO<sub>2</sub>(l) suggests that in these instances intermediate CO<sub>2</sub> complexes were formed. Such complexes, not stabilized by steric bulk, are open to attack by additional CO<sub>2</sub>, ultimately leading to reductive disproportionation to CO and CO<sub>3</sub><sup>2-</sup>. The use of steric bulk to stabilize highly reactive CO<sub>2</sub> complexes is clearly important.

But the results for the Ni triad provide the most dramatic illustration of the importance of electronic factors in CO<sub>2</sub> coordination. The compound [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>), which in solution is in equilibrium with Ni(N<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>, readily forms the modestly stable compound Ni(η<sup>2</sup>-CO<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> with CO<sub>2</sub>(g)<sup>3</sup> or CO<sub>2</sub>(l). It does not matter whether the CO<sub>2</sub> is dry or wet. The analogous Pd complex, Pd(PCy<sub>3</sub>)<sub>2</sub>, is unreactive toward either dry or wet CO<sub>2</sub>(l). And the complex Pt(PCy<sub>3</sub>)<sub>2</sub>, while unreactive toward dry CO<sub>2</sub>(l), reacts with wet CO<sub>2</sub>(l) to afford *trans*-PtH(O<sub>2</sub>COH)(PCy<sub>3</sub>)<sub>2</sub>.

Although the preparation of new, stable, isolable M-CO<sub>2</sub> complexes has not been realized in this initial study, we are encouraged by the ease with which we were able to prepare the known complex Ni(η<sup>2</sup>-CO<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> with CO<sub>2</sub>(l), rather than CO<sub>2</sub>(g), and by the ease with which we were able to screen

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transition-metal systems for their reactivity toward CO<sub>2</sub> through the use of CO<sub>2</sub>(l).

**Acknowledgment.** We thank Johnson Matthey, Inc., Malvern, PA, for the loan of the precious metal salts used in this work. This work was supported by the National Science Foundation (CHE80-09671).

**Registry No.** IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>, 15695-36-0; IrMe(CO)(PPh<sub>3</sub>)<sub>2</sub>,

53248-08-1; IrPh(CO)(PPh<sub>3</sub>)<sub>2</sub>, 25037-18-7; IrMo(O<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 82469-62-3; IrPh(O<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 53401-83-5; [RhH(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>), 69302-51-8; [Ni(PCy<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(μ-N<sub>2</sub>), 21729-50-0; Pd(PCy<sub>3</sub>)<sub>2</sub>, 33309-88-5; Pt(PCy<sub>3</sub>)<sub>2</sub>, 55664-33-0; Mo(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>, 73690-53-6; W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>, 73690-56-9; [Co(PPh<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(μ-N<sub>2</sub>), 33541-16-1; [Co(PEt<sub>2</sub>Ph)<sub>3</sub>]<sub>2</sub>(μ-N<sub>2</sub>), 33540-72-6; Na[Co(N<sub>2</sub>)(PEt<sub>2</sub>Ph)<sub>3</sub>], 33540-73-7; CO<sub>2</sub>, 124-38-9; IrMe(OCO<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 82469-63-4; IrPh(OCO<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, 82469-64-5; Ni(CO<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>, 57307-01-4; *trans*-PtH(O<sub>2</sub>COH)(PCy<sub>3</sub>)<sub>2</sub>, 82469-65-6; WH(O<sub>2</sub>COH)(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>, 82482-84-6.

## Fission Fragment Ionization Mass Spectrometry of Alamethicin I

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**Abstract:** Positive and negative Cf-252 fission fragment ionization spectra have been obtained for a natural and a synthetic sample of alamethicin I. The positive spectra of the two samples are identical to within an experimental error, and the negative spectra are identical except for the presence of a trace amount of impurity in the natural sample. The spectra provide strong evidence that the natural and synthetic samples are identical and thus that natural alamethicin I has the same structure as the known structure of the synthetic sample. The fragmentation occurring in the positive ion spectra is analyzed, and several series of sequence ions are identified. Reaction mechanisms producing the several series of sequence ions are suggested. Two of the sequence ions series involve addition of sodium ion to the alamethicin I molecule followed by fragmentation with retention of the sodium in the charged fragment.

Alamethicin (ALA)<sup>2</sup> is a peptide antibiotic produced by the fungus *Trichoderma viride*.<sup>3</sup> The primary interest in alamethicin stems from the fact that it affects the electrical properties of artificial bilayer membranes.<sup>4,5</sup> Some controversy has surrounded the elucidation of the structure of natural alamethicin,<sup>6</sup> which is a mixture of closely related compounds. Using the solid-phase technique,<sup>7</sup> one of us has recently concluded the chemical synthesis of the major component of alamethicin (ALA I) and has demonstrated identity of the synthetic with the natural product.<sup>8</sup>

Rinehart and co-workers<sup>9</sup> have made an extensive investigation of alamethicin using various mass spectrometric procedures, and their work provides strong evidence concerning the amino acid sequences in alamethicin I and II. Our main analytical goal in the work reported here is to demonstrate by fission fragment ionization mass spectrometry that separated and purified alamethicin I from natural sources is identical with synthesized alamethicin I. Such a comparison provides further evidence about the structure of natural alamethicin I. Fission fragment ionization

mass spectrometry<sup>10,11</sup> has been little used for the determination of the identity and structure of peptides, and consequently we give the results of our findings. In addition, we present details of the novel and interesting ionic chemistry giving rise to the observed spectra.

At present there exists only a very limited set of published data on polypeptides using fission fragment ionization mass spectrometry<sup>10-12</sup> or the related ionization techniques involving bombardment by keV ions<sup>13</sup> and intense laser pulses.<sup>14</sup> Macfarlane and co-workers have given in the open literature the spectra of two peptides, β-endorphin<sup>12</sup> and gramicidin A.<sup>10</sup> The spectrum of the 31-residue peptide β-endorphin covers the mass range from 900 to the quasi-molecular ion region at *m/z* 3487 ((M + Na)<sup>+</sup>). This spectrum is remarkable in that a distinct (M + Na)<sup>+</sup> ion is observed (signal to noise fluctuation ratio of approximately 20:1), while virtually no fragmentation is seen above *m/z* 900. The hints of fragment ion peaks that are to be seen have very low signal to noise fluctuation ratios (~1:1). The spectrum given for gramicidin A (15 residues) is restricted to the molecular ion region where (M + Na)<sup>+</sup> ions at *m/z* 1904 and 1918, respectively, are observed for the two variants studied. Macfarlane and co-workers also describe<sup>10</sup> certain aspects of the spectra of γ-glutathione (six residues) and a series of di- and tripeptides.

Positive and negative mass spectra for the tripeptide Ala-Ala-Ala have been obtained in this laboratory.<sup>11</sup> Quasi-molecular ions are observed in the positive ion spectrum, and the fragmentation is representative of the peptide structure. By contrast,

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(2) Abbreviations: ALA, alamethicin; Aib, α-aminoisobutyric acid; Phol, phenylalaninol.

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