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Photoelectron Spectroscopic Study of the Bonding in Tetracarbonyl(ethylene)iron

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The iron $2p_{3/2}$, carbon 1s, and oxygen 1s binding energies of gaseous $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ have been measured. Atomic charge calculations based on binding energy shifts indicate that the ethylene group of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ is negatively charged. Interpretation of the published UPS spectrum of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ with the aid of core binding energy shifts leads to the following conclusions: (1) There is significant σ interaction between the ethylene ligand and the $\text{Fe}(\text{CO})_4$ group of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$. (2) The energy of the (d_{xy} , $d_{x^2-y^2}$) orbitals of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ is affected by the two equatorial CO ligands and the ethylene ligand to the same extent as the energy of the (d_{xy} , $d_{x^2-y^2}$) orbitals of $\text{Fe}(\text{CO})_5$ is affected by three equatorial CO ligands. (3) The total back-bonding of the (d_{xz} , d_{yz}) orbitals of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ is less than that of $\text{Fe}(\text{CO})_5$, as expected from the orthogonality of these orbitals and the π^* orbital of coordinated C_2H_4 in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$.

Introduction

We have previously reported a gas-phase X-ray photoelectron study of the three-membered-ring compounds ($\text{Fe}(\text{CO})_4$) $_{3-n}$ (CH_2) $_n$, where $n = 0-3$.¹ For one member of this series, $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$, we were unable to obtain good-quality spectra because the sample was highly contaminated with $\text{Fe}(\text{CO})_5$. The core binding energy of only the ethylene carbon atoms was determined unambiguously. Because $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ is an example of a relatively simple complex of an unsubstituted olefin, we felt that a more thorough study of this compound was warranted.

Results and Discussion

The core binding energies of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ and the related compounds $\text{Fe}(\text{CO})_5$,² C_2H_4 ,³ and cyclopropane⁴ are given in Table I. The C 1s photoelectron spectrum of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ is shown in Figure 1. The intensity of the CH_2 peak relative to the CO peak is 0.68 ± 0.19 .

Atomic Charges from the Potential Equation. Core binding energy differences between $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ and $\text{Fe}(\text{CO})_5$ and between $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ and $\text{c-C}_3\text{H}_6$ were used to estimate the atomic charges in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ by means of the equation⁵

$$\Delta E_B = k_A \Delta Q_A + \Delta V - \Delta E_R(A)$$

where $\Delta E_B(A)$ is the binding energy difference of atom A, k_A is a constant for that atom determined by the expectation value of the inverse of the radius of atom A,⁶ ΔQ_A is the difference in charge on atom A, ΔV is the difference in potential felt by atom A due to the charges of the other atoms, and $\Delta E_R(A)$ is the difference in the electronic relaxation energy of atom A. By the use of binding energy data for $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ and $\text{Fe}(\text{CO})_5$, equations for $\Delta E_B(\text{Fe})$, $\Delta E_B(\text{C}(\text{CO}))$, and $\Delta E_B(\text{O})$ were obtained. Atomic charges for $\text{Fe}(\text{CO})_5$ were taken from an ab initio calculation⁷ (in which the Fe, C, and O atomic charges were calculated to be 1.039+, 0.174+, 0.381-, respectively). A fourth equation, for $\Delta E_B(\text{CH}_2)$, was obtained from the C 1s binding energies of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ and $\text{c-C}_3\text{H}_6$. Atomic charges for $\text{c-C}_3\text{H}_6$ were assumed to be 0.1- for the carbon atoms and 0.05+ for the hydrogen atoms.⁸ A fifth equation was obtained by requiring the sum of all the charges in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ to be zero. Electron relaxation energies were calculated by the transition-state method,⁹ using the equivalent-cores approximation.¹⁰ Valence potentials for the relaxation energy calculations were obtained by using CNDO/2 wave functions.¹¹ The experimental geometry of $\text{c-C}_3\text{H}_6$ ¹² and symmetric idealized geometries for $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ ¹³ and $\text{Fe}(\text{CO})_5$ ¹⁴ were used. It was found that the calculated differences in relaxation energy of the Fe, C(CO), and O atoms in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ and $\text{Fe}(\text{CO})_5$ were less than 0.1 eV and thus

insignificant. The difference in the CH_2 carbon relaxation energy between $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ and $\text{c-C}_3\text{H}_6$ was calculated to be 1.13 eV. The five equations were solved by using for $\Delta E_R(\text{CH}_2)$ the calculated value, half the calculated value,¹⁵ and zero. From the results, given in Table II, it can be seen that the calculated charges are insensitive to the assumption regarding $\Delta E_R(\text{CH}_2)$.

Our earlier result,¹ that the CH_2 group bears a charge of $\sim 0.2-$ was confirmed. In addition, it can be seen that the Fe atom of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ has a slightly higher positive charge than in $\text{Fe}(\text{CO})_5$, even though a qualitative interpretation of the binding energy difference alone would indicate the opposite. The observed decrease in Fe binding energy on going from $\text{Fe}(\text{CO})_5$ to $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ is mainly a result of replacing a carbonyl group, in which the negative charge is on the relatively distant oxygen atom, by the negatively charged C_2H_4 group, in which the negative charge is relatively near the iron atom. Our calculations indicate that the CO ligands have essentially the same charge in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ as in $\text{Fe}(\text{CO})_5$ and that the C_2H_4 group is more negatively charged than the carbonyl group it replaces.

Interpretation of UPS Data Using XPS Results. The first three ionization potentials of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$,¹⁶ the first two ionization potentials of $\text{Fe}(\text{CO})_5$,¹⁷ and the first ionization

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Table I. Core Binding Energies (eV) of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$, $\text{Fe}(\text{CO})_5$, C_2H_4 , and $c\text{-C}_3\text{H}_6$

	Fe $2p_{3/2}$		C 1s		O 1s	
	E_B	fwhm ^a	E_B	fwhm	E_B	fwhm
$\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$	715.40 (2) ^b	1.39 (7)	293.53 (3)	1.41 (7) (CO)	539.81 (2)	1.62 (7)
$\text{Fe}(\text{CO})_5$ ^c	715.79 (4)	1.25 (9)	290.32 (3)	1.32 (11) (CH_2)	539.96 (2)	1.38 (5)
C_2H_4 ^d			293.71 (5)	1.27 (13)		
$c\text{-C}_3\text{H}_6$ ^e			290.88			
			290.6			

^a Full width at half-maximum. ^b Uncertainty in last digit indicated parenthetically. ^c Reference 2. ^d Reference 3. ^e Reference 4.

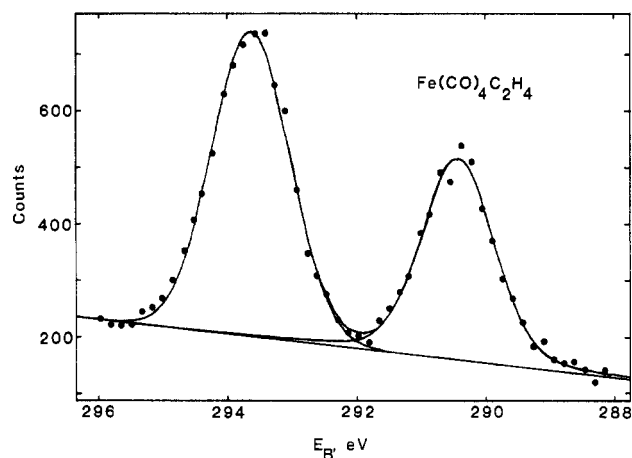
Table II. Calculated Atomic Charges in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$

	using $\Delta E_R(\text{CH}_2)$	using $1/2 \Delta E_R(\text{CH}_2)$	assuming $\Delta E_R(\text{CH}_2) = 0$
Q_{Fe}	1.15+	1.16+	1.17+
$Q_{\text{C}(\text{CO})}$	0.16+	0.16+	0.16+
Q_{O}	0.38-	0.38-	0.38-
$Q_{\text{C}(\text{CH}_2)}$	0.26-	0.31-	0.36-
Q_{H}	0.06+	0.08+	0.10+

Table III. Valence Ionization Potentials (eV) of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$, $\text{Fe}(\text{CO})_5$, and C_2H_4

	$\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ ^a	$\text{Fe}(\text{CO})_5$ ^b	C_2H_4 ^a
$\text{Fe}(d_{xy}, d_{x^2-y^2})$	8.38	8.6	
$\text{Fe}(d_{xz}, d_{yz})$	9.23	9.9	
$\text{C}=\text{C } \pi$	10.56		10.51

^a Reference 16. ^b Reference 17.

**Figure 1.** Carbon 1s photoelectron spectrum of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$.

potential of C_2H_4 ¹⁶ are listed in Table III. These data can be interpreted by using the core binding energies for these molecules and the approximation that shifts in strictly non-bonding atomic orbitals are eight-tenths of the corresponding shifts in core binding energy.¹⁸ Consider the molecular orbitals of the iron complexes that are largely comprised of the iron d_{xy} and $d_{x^2-y^2}$ orbitals. These orbitals are degenerate by symmetry in $\text{Fe}(\text{CO})_5$ and are practically degenerate when one of the equatorial CO groups is replaced by an ethylene molecule as in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$. The Fe $2p_{3/2}$ binding energy of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ is 0.39 eV less than that of $\text{Fe}(\text{CO})_5$. By subtracting 0.8 (0.39) from the $(d_{xy}, d_{x^2-y^2})$ ionization potential of $\text{Fe}(\text{CO})_5$, we obtain 8.3 eV, which is the value that the corresponding ionization potential of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ would have if the net interaction between the $(d_{xy}, d_{x^2-y^2})$ orbitals and the ligands were the same as in $\text{Fe}(\text{CO})_5$. We see that, within the uncertainty of the estimate (± 0.1 eV), the actual $(d_{xy}, d_{x^2-y^2})$ ionization potential of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ equals our estimate. Hence, we conclude that the net interaction between the $(d_{xy},$

$d_{x^2-y^2})$ orbitals and the three equatorial ligands is approximately the same in $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$.

By a similar calculation involving the (d_{xz}, d_{yz}) orbitals (degenerate by symmetry in $\text{Fe}(\text{CO})_5$ and practically degenerate in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$), we estimate that the (d_{xz}, d_{yz}) ionization potential of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ would be 9.6 eV if the total extent of (d_{xz}, d_{yz}) back-bonding were the same as in $\text{Fe}(\text{CO})_5$. We see that the actual (d_{xz}, d_{yz}) ionization potential is ~ 0.4 eV lower, corresponding to a relative destabilization of this orbital in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$. Similarly, using the $\text{C}=\text{C } \pi$ orbital ionization potentials and the appropriate C 1s binding energies, we determine that the C_2H_4 π orbital in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ is stabilized by ~ 0.5 eV relative to free ethylene.

The stabilization of the C_2H_4 π orbital indicates that there is distinct σ interaction between the π orbital of ethylene and one of the $(d_{xy}, d_{x^2-y^2})$ orbitals in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$. This conclusion is contrary to that of Oskam et al.,^{16,17} who ignored the effect of the change in charge of the ethylene carbon atoms and concluded, from the similarity of the C_2H_4 π -ionization potentials in the complex and the free ligand, that the C_2H_4 π orbital is not perturbed significantly by the $\text{Fe}(\text{CO})_4$ group. Worley et al.¹⁹ have pointed out the unreasonableness of this interpretation.

Our results show that the net $\sigma + \pi$ interaction between the $(d_{xy}, d_{x^2-y^2})$ orbitals and the equatorial ligands is approximately the same in $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$. It has been shown that the $\text{C}=\text{C}$ bond of the coordinated ethylene in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ lies in the equatorial plane of the molecule.¹³ If we assume that the σ -donor character of ethylene is the same as that of CO, we conclude that the extent of back-bonding from the $(d_{xy}, d_{x^2-y^2})$ orbitals to C_2H_4 is the same as to a CO molecule. If we more reasonably assume that the σ -donor character of ethylene is greater than that of CO (indeed, the proton affinity of ethylene is greater than that of carbon monoxide²⁰), we conclude that back-bonding from the $(d_{xy}, d_{x^2-y^2})$ orbitals is greater to C_2H_4 than to CO. Greater back-bonding to C_2H_4 is consistent with our finding that the Fe atom in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ is more positively charged than that in $\text{Fe}(\text{CO})_5$. On the other hand, the (d_{xz}, d_{yz}) orbitals are orthogonal to the π^* orbital of C_2H_4 in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$. Hence, these orbitals engage in back-bonding to only four ligands in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$, as opposed to five in $\text{Fe}(\text{CO})_5$. Although the total back-bonding by the (d_{xz}, d_{yz}) orbitals is reduced in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$, the back-bonding per CO is probably slightly greater. If we assume, in $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ relative to $\text{Fe}(\text{CO})_5$, that back-bonding to the axial CO groups is slightly increased and that back-bonding to the equatorial CO is slightly decreased, we rationalize our result that the CO groups in the two molecules have about the same average charge.

Experimental Section

Iron tetracarbonyl ethylene was prepared by the method of Murdoch and Weiss,²¹ in which $\text{Fe}_2(\text{CO})_9$ reacts with C_2H_4 under high pressure. The purification of the product requires that it be separated from the

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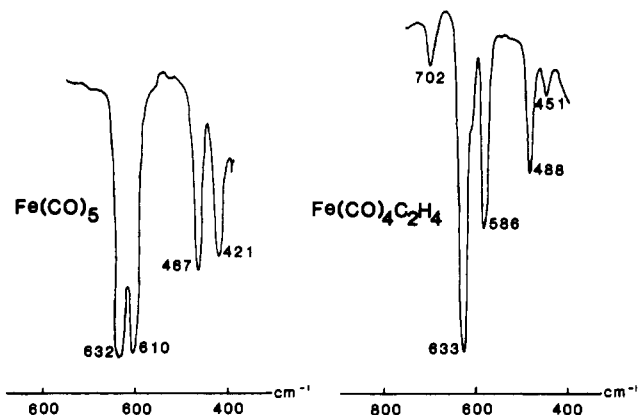


Figure 2. Metal-ligand stretch region of the infrared spectra of $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$.

large amount of $\text{Fe}(\text{CO})_5$ produced in the reaction. The compound has been reported to decompose on standing at room temperature and on vacuum transfer from one vessel to another.^{21,19} Van Dam and Oskam¹⁶ suggested that the $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ sample used in the UPS study of Baerends et al.¹⁷ was contaminated with $\text{Fe}(\text{CO})_5$ because of decomposition in the spectrometer. However, we have observed that the thermal and photochemical decomposition of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ results only in the production of $\text{Fe}_3(\text{CO})_{12}$ and C_2H_4 . It is possible that the sample of Baerends et al. had not been originally free of $\text{Fe}(\text{CO})_5$, as was also the case in our earlier XPS study.¹ Because of these prior difficulties in the preparation and handling of this important compound, the synthesis and characterization of $\text{Fe}(\text{C}-\text{O})_4\text{C}_2\text{H}_4$ are described in some detail below.

Diiron enneacarbonyl in pentane was treated with C_2H_4 at 50 atm for 48 h. The excess C_2H_4 was vented, and the mixture of $\text{Fe}(\text{CO})_5$

and $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ was separated from the solvent by fractional condensation on a vacuum line at -63°C . The $\text{Fe}(\text{CO})_5\text{-Fe}(\text{C}-\text{O})_4\text{C}_2\text{H}_4$ mixture was separated by reduced-pressure fractional distillation with a 15-cm Vigreux column, a 0°C condenser, and a four-arm fraction collector cooled to 0°C . Nitrogen was bled into the still pot to prevent bumping and to maintain the pressure at 12 mm. The majority of the material distilled at $19\text{--}26^\circ\text{C}$ and was primarily $\text{Fe}(\text{CO})_5$ contaminated with a small amount of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$. Iron tetracarbonyl ethylene was collected at $31\text{--}34^\circ\text{C}$. The middle portion of this fraction (bp $33\text{--}34^\circ\text{C}$) was distilled into a vial and stored in vacuo at -78°C in the dark prior to obtaining the XPS spectrum. The absence of $\text{Fe}(\text{CO})_5$ in the sample of $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ was confirmed by gas-phase infrared spectroscopy.²² Spectra were obtained on a Perkin-Elmer 597 infrared spectrometer with use of a 10-cm path length cell and a sample pressure of ~ 8 mm. The metal-ligand stretch regions of $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ are shown in Figure 2. The absence of bands at 610, 467, and 421 cm^{-1} in the infrared spectrum and the narrowness of the boiling range are our principal evidence that the $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ sample was free of $\text{Fe}(\text{CO})_5$.

Gas-phase X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA 36 spectrometer by a method described previously.² The vapor from $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ held at -25°C was passed into the gas cell of the spectrometer, which was at ambient temperature. The spectra obtained did not vary during the run. Spectra were calibrated by using the N_2 1s, Ne 1s, and Ne 2s reference peaks.

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Electron-Transfer Reactions of Copper(III)-Peptide Complexes with Ruthenium(II) Ammine and Copper(II)-Peptide Complexes

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The self-exchange rate constants for five copper(III, II) peptides have been determined by using the reactions of copper(III) α -aminoisobutyryl- α -aminoisobutyryl- α -aminoisobutyric acid with the copper(II) complexes. Copper(III)-peptide complexes are rapidly reduced by $\text{Ru}(\text{NH}_3)_6^{2+}$, $\text{Ru}(\text{NH}_3)_5(\text{py})^{2+}$, and $\text{Ru}(\text{NH}_3)_5(\text{pic})^{2+}$ at rates that are accurately predicted from the Marcus theory and the determined self-exchange rate constants for copper(III, II) peptides and the ruthenium complexes. The activation parameters for the reactions of copper(III) α -aminoisobutyryl- α -aminoisobutyryl- α -aminoisobutyramide with $\text{Ru}(\text{NH}_3)_6^{2+}$ are $\Delta H^\ddagger = 1.5 \pm 0.3\text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -21 \pm 2\text{ cal K}^{-1}\text{ mol}^{-1}$. For the corresponding reaction with $\text{Ru}(\text{NH}_3)_5(\text{py})^{2+}$, the values are $\Delta H^\ddagger = 1.8 \pm 0.6\text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -25 \pm 2\text{ cal K}^{-1}\text{ mol}^{-1}$. The data support an outer-sphere mechanism of electron transfer for all the reactions.

Introduction

Copper(III) peptides, which are d^8 low-spin square-planar complexes,¹⁻³ undergo electron-transfer reactions by at least two different pathways. In the reductions with IrCl_6^{3-} and $\text{Fe}(\text{CN})_6^{4-}$ the extraordinary speed of the reactions (corresponding to an apparent self-exchange rate constant of approximately $10^8\text{ M}^{-1}\text{ s}^{-1}$ for $\text{Cu}(\text{III})\text{-Cu}(\text{II})$) strongly suggests inner-sphere mechanisms.^{4,5} In these cases chloride or cyanide

bridges between the metal centers can form readily along the open axial positions of the copper(III) complexes. Although only weak axial coordination occurs with copper, this appears to provide a favorable inner-sphere pathway for rapid electron transfer. On the other hand, the electron-exchange reaction of $\text{Cu}^{\text{III}}(\text{H}_2\text{Aib}_3)$ (I) with $\text{Cu}^{\text{II}}(\text{H}_2\text{Aib}_3)^-$ (see ref 6 for abbreviations) was measured directly by ^1H NMR line broadening⁷ and gave a self-exchange rate constant of $5.5 \times 10^4\text{ M}^{-1}$

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- (6) Abbreviations used: G, glycol; A, alanyl; V, valyl; Aib, α -aminoisobutyryl; OCH₃, terminal ester; a, terminal amide; C, cyclo(β -alanyl-glycyl- β -alanyl-glycyl); H_nL refers to a peptide ligand with n deprotonated peptide nitrogens coordinated to the metal; py, pyridine; pic, 4-methylpyridine.
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