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Complexes of Trivalent Phosphorus Derivates. IV. Metal Carbonyl Complexes of Cis-Bis-1,2,-(Diphenylphosphino) Ethylene.[1]

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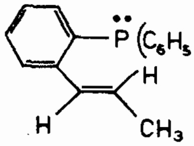
Reactions of various metal carbonyl derivatives with cis-*bis-1,2-(diphenylphosphino)ethylene, $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ (designated as Pf=Pf) are reported. In all cases studied this ligand acts as chelating ditertiary phosphine without the carbon-carbon double bond coordinating to the metal atom. The proton n.m.r. spectra of some of the complexes show a large downfield shift of the olefinic protons suggesting a ring current in the chelate ring. New compounds prepared and characterized in this work are $(Pf=Pf)M(CO)_4$ (M = Cr, Mo, and W), $(Pf=Pf)Fe(CO)_3$, $(Pf=Pf)Ni(CO)_2$, and $C_5H_5MnCO(Pf=Pf)$.*

Introduction

Recently reactions between various metal carbonyls and the olefinic phosphines 2-propenylphenyldiphenylphosphine $(C_3H_5)C_6H_4P(C_6H_5)_2$: (I)[4] and 9-phenyl-9-phosphabicyclo[4,2,1] nonatriene ($C_8H_8PC_6H_5$: (II))[1] were investigated in an attempt to assess the relative tendencies for tricovalent phosphorus atoms and carbon-carbon double bonds to complex with transition metals. These studies, particularly the one with 9-phenyl-9-phosphabicyclo[4,2,1] nonatriene, clearly indicated a much greater tendency for tricovalent phosphorus atoms than carbon-carbon double bonds to bond to transition metals.

In a continuation of this study we have now investigated the reaction of *cis*-bis(1,2-diphenylphosphino)-ethylene ((III): designated as Pf = Pf)[5] with the various metal carbonyl derivatives. This ligand can either act as a chelating ditertiary phosphine, or an olefin. Furthermore in principle it could act simultaneously as both since the two phosphorus atoms and the carbon-carbon double bond might be expected to form a delocalized system capable of π-bonding to a transition metal. This paper reports six metal carbonyl complexes of *cis*-bis-(1,2-diphenylphosphino)ethylene (III) (Table I). In all of these complexes the unsaturated ditertiary phosphine (III) behaves as a bidentate chelating ligand using only the phosphorus atoms and forming complexes completely analogous to those formed by the closely related saturated ditertiary phosphine 1,2-bis-(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ ((IV): designated as Pf–Pf)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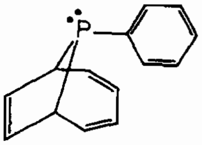
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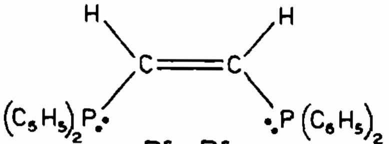
Pf=Pf
III

Results and Discussion

The techniques for preparing the new Pf = Pf complexes were completely analogous to those suitable for preparing related metal carbonyl complexes of other tertiary phosphines.[6] Rather complex and ill-defined fractional crystallization procedures were used to free the Pf = Pf complexes from excess ligand. Recovery of pure products appeared to be inefficient. The compounds $(Pf=Pf)M(CO)_4$ ((V): M = Cr, Mo, and W) were obtained by simply heating the ligand (III) with the corresponding metal hexacarbonyl. Treatment of the ligand (III) with $Ni(CO)_4$ at room temperature gave the nickel complex $(Pf=Pf)Ni(CO)_2$. Ultraviolet irradiation[7] was used to convert $C_5H_5Mn(CO)_3$ into $C_5H_5MnCO(Pf=Pf)$ (VI) by reaction with the ligand (III); the non-chelate bridging derivative $C_5H_5Mn(CO)_2(Pf=Pf)Mn(CO)_2C_5H_5$ was not found as a by-product.[8] The iron complex $(Pf=Pf)Fe(CO)_3$ was prepared from the ligand (III) and $Fe_2(CO)_9$ at room temperature. Use of the less reactive $Fe(CO)_5$ made a higher reaction

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[1] For part III of this series see R. B. King and K. H. Pannell, *Inorg. Chem.*, 7, 273 (1968).

[2] Fellow of the Alfred P. Sloan Foundation, 1967-1969.

[3] Postdoctoral research associate supported by Grant AF-AFOSR-1211-67 of the Air Force Office of Scientific Research from January, 1967, to October, 1967.

[4] L. V. Interrante, M. A. Bennett, and R. S. Nyholm, *Inorg. Chem.*, 5, 2212 (1966).

[5] A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, 86, 2299 (1964).

[6] T. A. Manuel, *Adv. Organometal. Chem.*, 3, 181 (1965).

[7] For a discussion of the ultraviolet irradiation of $C_5H_5Mn(CO)_3$ with various ligands see W. Strohmeier and J. F. Guttenberger, *Z. Naturforsch.*, *18b*, 667 (1963) and J. Lewis, R. S. Nyholm, A. G. Osborne, S. S. Sandhu, and M. H. B. Stiddard, *Chem. Ind.*, (London), 1398 (1963).

[8] The saturated analogue bis(1,2-diphenylphosphino)ethane formed both $C_5H_5Mn(CO)_2(Pf\text{-}Pf)Mn(CO)_2C_5H_5$ and $C_5H_5MnCO(Pf\text{-}Pf)$ upon ultraviolet irradiation with $C_5H_5Mn(CO)_3$. See R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, 26, 1977 (1964).

Table I. Metal Carbonyl Derivatives of *cis*-bis-1,2-(diphenylphosphino) ethylene [a]

Compound [a]	Color	m.p.		Analyses %				
				C	H	P	O	M
$(Pf=Pf)Cr(CO)_4$	yellow	152-153°	Calcd.	64.3	4.0	11.1	11.4	
			Found	64.4	4.2	10.9	11.2	
$(Pf=Pf)Mo(CO)_4$	pale yellow	174-176°	Calcd.	59.6	3.7	10.2	10.6	
			Found	60.4	4.2	9.8	10.4	
$(Pf=Pf)W(CO)_4$	pale yellow	178-180°	Calcd.	52.0	3.2	8.9	9.3	
			Found	52.1	3.2	9.1	9.4	
$(Pf=Pf)Fe(CO)_3$	yellow-orange	139-140°	Calcd.	65.0	4.1	11.6	8.9	10.4
			Found	65.6	4.2	11.5	8.7	10.1
$(Pf=Pf)Ni(CO)_2$	yellow	154-157°	Calcd.	65.8	4.3	12.1	6.3	
			Found	66.2	4.8	11.9	6.7	
$C_5H_5MnCO(Pf=Pf)$	orange	225-226°	Calcd.	69.9	5.1	11.6	3.0	10.3
			Found	70.2	5.2	11.8	3.0	10.1

[a] Pf = Pf refers to *cis*-bis-1,2-(diphenylphosphino)ethylene.

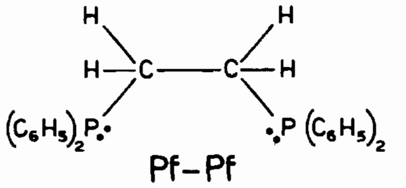
temperature necessary. This led to some decomposition and a more complex reaction mixture from which pure product could not be obtained.

The ν(CO) frequencies in these new metal carbonyl complexes of *cis*-bis(1,2-diphenylphosphino)ethylene (III) were almost identical to those of analogous metal carbonyl complexes of bis(1,2-diphenylphosphino)-ethane (IV) indicating similar structures (see Table II). In most cases the ν(CO) frequencies of the complexes of the unsaturated ditertiary phosphine Pf = Pf (III) occurred at very slightly higher values than the corresponding ν(CO) frequencies of completely analogous complexes of the saturated ditertiary phosphine Pf—Pf (IV). This may be an indication of a very slightly higher π-acceptor strength of the unsaturated ditertiary phosphine (III) than of the saturated ditertiary phosphine (IV). This could arise from either an inductive effect of the more electronegative sp^2 carbon atoms or the presence of empty antibonding orbitals in the carbon-carbon double bond. The four ν(CO) frequencies were observed in the compounds $(Pf=Pf)M(CO)_4$ as expected for the two A_1, the B_1, and the B_2 modes of an octahedral *cis*-$L_2M(CO)_4$ derivative.

Table II. ν(CO) Frequencies of Some Chelating Ditertiary Phosphine Complexes of Metal Carbonyls, cm.$^{-1}$

Compound [a]	Medium [b]	ν(CO) frequencies	Refer.
$(Pf=Pf)Cr(CO)_4$	C_6H_6	2011, 1915, 1902, 1886	c
$(Pf-Pf)Cr(CO)_4$	$C_2H_4Cl_2$	2009, 1914, 1899, 1877	d
$(Pf=Pf)Mo(CO)_4$	C_6H_6	2022, 1925, 1912, 1897	c
$(Pf-Pf)Mo(CO)_4$	$C_2H_4Cl_2$	2020, 1919, 1907, 1881	d
$(Pf=Pf)W(CO)_4$	C_6H_6	2022, 1920, 1906, 1890	c
$(Pf-Pf)W(CO)_4$	$C_2H_4Cl_2$	2016, 1912, 1901, 1876	d
$(Pf=Pf)Fe(CO)_3$	CH_2Cl_2	1988, 1920, 1897	c
$(Pf-Pf)Fe(CO)_3$	$CHCl_3$	1992, 1923, 1901	e
$(Pf=Pf)Ni(CO)_2$	C_6H_6	2010, 1940	c
$(Pf-Pf)Ni(CO)_2$	$CHCl_3$	2006, 1945	f
$C_5H_5MnCO(Pf=Pf)$	CH_2Cl_2	1840	c
$C_5H_5MnCO(Pf-Pf)$	CS_2	1834	g

[a] Pf = Pf refers to *cis*-bis-1,2-(diphenylphosphino)ethylene, $(C_5H_5)_2PCH=CHP(C_6H_5)_2$. Pf—Pf refers to bis-1,2-(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. [b] The solvent used for the spectrum is indicated as follows: C_6H_6 = benzene, $C_2H_4Cl_2$ = 1,2-dichloroethane, CH_2Cl_2 = dichloromethane, $CHCl_3$ = chloroform, CS_2 = carbon disulfide. [c] This work. [d] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961). [e] T. A. Manuel, *Inorg. Chem.*, *2*, 854 (1963). [f] G. R. Van Hecke and W. de Horrocks Jr., *Inorg. Chem.*, *5*, 1960 (1966). [g] R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, *26*, 1977 (1964).



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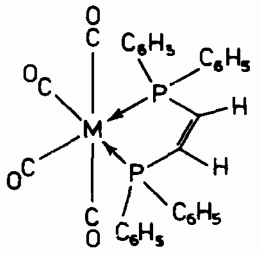
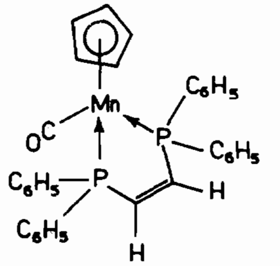


V



VI

Besides the ν(CO) frequencies the infrared spectra of benzene solutions of the $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ complexes exhibit bands at 1428 ± 3, 1087 ± 3, and 725 ± 3, cm^{-1} arising from the ligand.

The proton n.m.r. spectra of several of the new complexes of *cis*-bis(1,2-diphenylphosphino)ethylene are listed in Table III. In the free ligand (III) the aromatic proton resonance hides the much weaker olefinic proton resonance. In the proton n.m.r. spectrum of the compounds $(Pf=Pf)M(CO)_4$ (M = Cr, Mo, and W) both the aromatic and olefin proton resonances are shifted downfield from their positions in the free ligand III. However, the downfield shift of the olefinic protons of the complexes $(Pf=Pf)M(CO)_4$ (M = Cr, Mo, and W) is enough greater than that of the aromatic protons that the olefinic proton resonance is no longer hidden by the aromatic proton resonance. The double doublet pattern of the olefinic proton resonance appears to arise from unequal coupling (J_1 = 41-48 c.p.s. and J_2 = 8-15 c.p.s. in the case of the $(Pf=Pf)M(CO)_4$ compounds) of the olefinic proton with the differently situated phosphorus atoms. The low chemical shifts of the olefinic protons in the $(Pf=Pf)M(CO)_4$ ((V): M = Cr, Mo, and W) compounds may be a consequence of a ring current in the potentially aromatic chelate ring containing the metal

able III. Proton N.M.R. Spectra of Some *cis*-bis-1,2-(diphenylphosphino)ethylene Derivatives

ompound [a]	Solvent	$\tau(C_6H_5)$ [b]	Olefinic protons		
			$\tau(=CH)$	$J_1(PCH=)$ [c]	$J_2(PC=CH)$ [c]
f = Pf	$CDCl_3$	2.81	2.77	$J_1 + J_2$ = 28 c.p.s.	
Pf = Pf)Cr(CO)$_4$	Me_2CO	2.1, 2.25	1.33	48	11
Pf = Pf)Mo(CO)$_4$	Me_2CO	2.1, 2.25	1.48	47	8
Pf = Pf)W(CO)$_4$	Me_2CO	2.1, 2.25	1.42	41	15
Pf = Pf)Ni(CO)$_2$	Me_2CO	2.2, 2.3	~2.0		20?
Pf = Pf)Fe(CO)$_3$	Me_2CO	2.46	[d]		
$_5H_5$Mn(CO)(Pf = Pf)	$Me_2CO + CDCl_3$	2.56, 2.68, 2.79	2.09 (?) [e]	($\tau(C_5H_5)$ = 5.90)	

Pf = Pf refers to *cis*-bis-1,2-(diphenylphosphino)ethylene, $(C_6H_5)_2PCH=CHP(C_6H_5)_2$. [b] Positions of the peaks in the complex phenyl esonances were noted. [c] Coupling constants are given in c.p.s. [d] This resonance could not be unequivocally observed. The assignment of this broad resonance was uncertain. No coupling constants were observed.

atom, the two phosphorus atoms, and the two olefinic sp^2 carbon atoms. In a few cases the n.m.r. spectra were so weak that the weak olefinic proton resonances could not be unambiguously identified.

We also investigated reactions between Pf = Pf (III) and other metal carbonyl derivatives besides those giving the compounds listed in Table I. The following additional results were obtained:

(1) $Mn_2(CO)_{10}$ (hexane, 25°, 5 hr., U.V. irradiation): A complex mixture of yellow to yellow-orange products was obtained. Complete separation into pure compounds was not achieved.

(2) $C_5H_5V(CO)_4$ (dibutyl ether, boiling point, 19 hr.): Very air-sensitive brown products were obtained which appeared to be $C_5H_5V(CO)_2$(Pf = Pf) (ν(CO) = 1866 and 1790 cm^{-1}) and C_5H_5V(Pf = Pf)$_2$.

(3) $C_7H_8Mo(CO)_3$ (benzene, 25°, 19 hr.): A fairly low yield of (Pf = Pf)Mo(CO)$_4$ ((V): M = Mo) was obtained. Similar reactions of $C_7H_8Mo(CO)_3$ with other tricovalent phosphorus derivatives to give $L_2Mo(CO)_4$ compounds have been reported.[1,9]

(4) $C_5H_5Co(CO)_2$ (benzene, 80°, 2 hr.): A low yield of deep red unstable crystals, m.p. 118-121°, were obtained which appear to be C_5H_5Co(Pf = Pf) (see Experimental Section).

(5) $[C_5H_5NiCO]_2$ (benzene, 25-50°) : A small amount of (Pf = Pf)Ni(CO)$_2$ was detected in the reaction mixture from the ν(CO) frequencies in the infrared spectrum. A similar reaction between $[C_5H_5NiCO]_2$ and tris(dimethylamino)phosphine gives the related dicarbonyl derivative $[(Me_2N)_3P]_2Ni(CO)_2$.[9]

Experimental Section

Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra (Table II) were taken in benzene or dichloromethane solution and recorded on a Perkin-Elmer Model 621 spectrometer. Proton n.m.r. spectra (Table III) were taken in the indicated solvents and recorded on a Varian HA-100 spectrometer at 100 Mc. or a Varian A-60 spectrometer at 60 Mc.

The ligand *cis*-bis(1,2-diphenylphosphino)ethylene (III) was obtained in ~45% yield as white crystals, m.p. 115-117°, from lithium diphenylphosphide and *cis*-1,2-dichloroethylene in boiling tetrahydrofuran by the published procedure.[5] The lithium diphenylphoshide was obtained from triphenylphosphine and lithium metal in tetrahydrofuran solution followed by treatment with *t*-butyl chloride to selectively destroy the phenyllithium byproduct.[10] The proton n.m.r. spectrum of the ligand (III) was identical to that reported in the literature.[5]

The $Fe_2(CO)_9$ used in this work was prepared by ultraviolet irradiation of an acetic acid solution of $Fe(CO)_5$ in a water-cooled reactor.[11] The other metal carbonyl derivatives used in this work were commercial products.[12] Tetrahydrofuran and di-*n*-butyl ether were purified by distillation over lithium aluminum hydride.

A nitrogen atmosphere was routinely provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, (c) admission to evacuated vessels. Ultraviolet irradiations were carried out with a 125 watt mercury vapor lamp containing 7 mm. argon pressure[13] and protected from the reaction mixture by a quartz sleeve.

(Pf = Pf)Mo(CO)$_4$. A mixture of 0.88 g. (3.33 mmoles) of $Mo(CO)_6$ and 1.32 g. (3.33 mmoles) of $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ was boiled under reflux 37 hr. in 50 ml. of methylcyclohexane. After cooling to room temperature, solvent was removed from the reaction mixture at 25°/0.1 mm. After repeated fractional crystallization from mixtures of benzene and hexane 0.71 g. (35% yield) of pale yellow crystalline (Pf = Pf)-Mo(CO)$_4$, m.p. 174-176°, was obtained.

(Pf = Pf)Cr(CO)$_4$. A mixture of 0.73 g. (3.3 mmoles) of $Cr(CO)_6$ and 1.32 g. (3.33 mmoles) of $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ was boiled under reflux 25 hr. in ~50 ml. of di-n-butyl ether. After cooling to room temperature, the reaction mixture was concentrated to ~15 ml. at 25°/0.1 mm. and product obtained by fractional precipitation with petroleum ether. The crude product was recrystallized once from a mixture of diethyl ether

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(9) R. B. King, *Inorg. Chem.*, 2, 936 (1963).

(10) A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, 27, 1001 (1962).

(11) This procedure is a modification of the procedure described by R. B. King, *Organometal. Syn.*, *1*, 93 (1965). See also E. H. Braye and W. Hübel, *Inorg. Syn.*, *8*, 178 (1966).

(12) The following commercial sources were used: (a) $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$: Pressure Chemical Company, Pittsburgh, Pennsylvania; (b) $C_5H_5Mn(CO)_3$: Ethyl Corporation, New York, New York; (c) $Fe(CO)_5$: Antara Division of General Aniline and Film, Corp., New York, New York; (d) $Ni(CO)_4$: Matheson Company, East Rutherford, New Jersey.

(13) This ultraviolet irradiation equipment is available from Nester-Faust Manufacturing Corp., Newark, Delaware.

and petroleum ether and then a second time from a mixture of chloroform and methanol to give 0.69 g. (37% yield) of yellow crystalline (Pf = Pf)Cr$(CO)_4$, m.p. 152.5-153.5°.

(Pf = Pf)W(CO)₄. A mixture of 1.24 g. (3.3 mmoles) of $W(CO)_6$ and 1.32 g. (3.33 mmoles) of $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ in ~50 ml. of di-*n*-butyl ether was boiled under reflux 45 hr. with stirring. The dirty-brown solution was then filtered hot and the brown filtrate cooled at −10° for several hours. The yellow-brown crystals were filtered and crystallized three times from mixtures of benzene and hexane to give 1.09 g. (48% yield) of yellow crystalline (Pf = Pf)-W$(CO)_4$, m.p. 178-180°.

(Pf = Pf)Fe$(CO)_3$. A mixture of 0.52 g. (1.43 mmoles) of $Fe_2(CO)_9$ and 1.32 g. (3.33 mmoles) of $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ in 100 ml. of hexane was subjected to ultraviolet irradiation for 21 hr. Solvent was then removed from the reaction mixture at ~25°/40 mm. The residue was extracted with a minimum of benzene and the filtered benzene extracts evaporated at room temperature. The residues were subjected to two fractional crystallizations from mixtures of benzene and hexane precipitating the product by keeping the solutions two weeks at −10°. A total of 0.165 g. (11% yield, based or iron introduced) of yellow-orange needles of (Pf = Pf)Fe$(CO)_3$, m.p. 139.5°-140.5°, was obtained.

(Pf = Pf)Ni$(CO)_2$. A solution of 1.0 g. (2.52 mmoles) of $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ in a mixture of 10 ml. of benzene and 30 ml. of hexane was treated with excess (~1 ml.) of $Ni(CO)_4$. Vigorous bubbling occurred with the precipitation of a yellow solid after about five minutes. This yellow solid was combined with additional material obtained by evaporating the reaction mixture at room temperature. The mixed yellow solids were crystallized from a mixture of benzene and hexane to give 0.57 g. (44% yield) of yellow (Pf = Pf)Ni$(CO)_2$, m.p. 154-157°.

C_5H_5MnCO(Pf = Pf). A solution of 0.81 g. (4.0 mmoles) of $C_5H_5Mn(CO)_3$ and 1.58 g. (4.0 mmoles) of $(C_6H_5)_2PCH=CHP(C_6H_5)_2$ in ~200 ml. of ethanol was exposed to ultraviolet irradiation with stirring for 23 hr. Solvent was then removed at 25°/40 mm. The resulting orange solid was recrystallized three times from mixtures of dichloromethane and hexane to give 0.77 g. (35% yield) of orange C_5H_5MnCO(Pf = Pf), m.p. 222-224°. The analytical sample, m.p. 225-226°, was obtained by a further recrystallization from an acetone-hexane mixture.

Reaction between $C_5H_5Co(CO)_2$ and $(C_6H_5)_2PCH=CHP(C_6H_5)_2$. A mixture of 0.36 g. (2.0 mmoles) of $C_5H_5Co(CO)_2$ and 0.79 g. (2.0 mmoles) of $(C_6H_5)_2$-$PCH=CHP(C_6H_5)_2$ in 50 ml. of benzene was boiled under reflux 105 minutes with stirring. After cooling to room temperature, solvent was removed at ~25°/40 mm. The solid residue was recrystallized once from a mixture of benzene and hexane and a second time from a mixture of dichloromethane and methanol to give 0.08 g. of dark red crystals, m.p. 118-121°, indicated by analyses to be somewhat impure C_5H_5Co-(Pf = Pf) (Calcd.: C, 71.6; H, 5.2; P, 11.9; O, 0.0. Found: C, 70.8; H, 6.7; P, 11.7; O, 3.9). This compound decomposes readily in solution making recrystallization rather unsatisfactory. The infrared spectrum in CH_2Cl_2 solution showed no ν(CO) frequencies.

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