

Metallacycloalkanes. 9.¹ Synthesis of the First Mixed Nickelacyclopentane via Oxidative Coupling of 3,3-Dimethylcyclopropene and Methyl Acrylate

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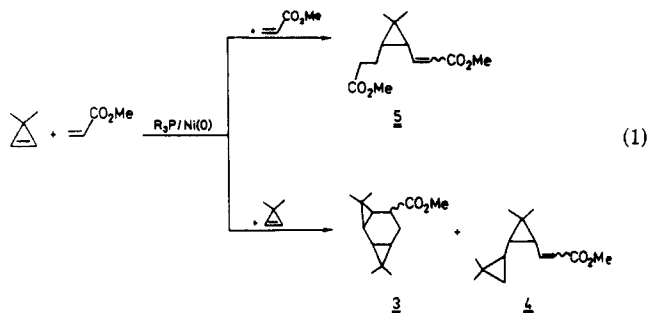
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4-(Triphenylphosphane)-*cis*-2,2-dimethyl-5-(methoxycarbonyl)-4-nickelabicyclo[3.1.0]hexane (1) has been synthesized from bis(triphenylphosphane)(η^2 -methyl acrylate)nickel [(tpp)₂Ni(mac)] and 3,3-dimethylcyclopropene [dmcp] in 65% isolated yield. Compound 1 exhibits an unusual structure involving coordination of the methoxycarbonyl group. For further characterization, compound 1 has been transformed into the square-planar 4-[ethylenebis(dimethylphosphane)]-*cis*-2,2-dimethyl-5-(methoxycarbonyl)-4-nickelabicyclo[3.1.0]hexane (2) by displacement of triphenylphosphane with ethylenebis(dimethylphosphane) (dmpe). Structure determination of compounds 1 and 2 in solution is based on molecular weight determination (1) and mass, IR, and ¹H and ¹³C NMR spectroscopy. Compound 1 catalyzes the cotrimerization of dmcp and mac with almost identical reactivity and selectivity as the previously known "in situ" catalyst obtained by mixing bis(cycloocta-1,5-diene)nickel [Ni(cod)₂] and tpp in a molar ratio of 1:1, indicating that 1 may be regarded as an intermediate in this reaction that seems to be catalyzed by the (tpp)Ni fragment.

Introduction

Catalytic processes transforming simple unsaturated hydrocarbons into industrially important intermediates are of considerable interest.² In this context, new cycloaddition reactions proceeding under mild conditions without generating undesired byproducts appear to be particularly attractive.³ In recent years many observations have been made giving evidence that these processes may proceed via metallacyclic intermediates.⁴ Especially the role of metallacyclopentanes as intermediates in transition-metal-catalyzed reactions involving dmcp,⁵ methylenecyclopropane,⁶ norbornadiene,^{6a} and ethylene⁷ has been studied in detail. Furthermore, metallacyclopentanes have been proposed as intermediates in the nickel(0)-catalyzed codimerization reactions of methylenecyclopropane with norbornadiene,⁸ mac, or other electron-deficient alkenes⁹ as well as for the cotrimerization of dmcp with mac.¹⁰ The

latter reaction is catalyzed by triorganylphosphane or triorganyl phosphite modified nickel(0) compounds with the product distribution being determined by the nature of the phosphorus ligand (eq 1).



We have now found that bis(triphenylphosphane)(η^2 -methyl acrylate)nickel [(tpp)₂Ni(mac)] reacts smoothly with dmcp to afford 4-(triphenylphosphane)-*cis*-2,2-dimethyl-5-(methoxycarbonyl)-4-nickelabicyclo[3.1.0]hexane (1), the first example of a stable "mixed" nickelacyclopentane. Compound 1 can be transformed into the corresponding nickelacyclopentane derivative 2 by displacement of tpp with ethylenebis(dimethylphosphane) (dmpe). In this paper we report the synthesis, structure elucidation, and characterization of compounds 1 and 2. The role of compound 1 as an intermediate in the above-mentioned catalytic cotrimerization (eq 1) will be briefly discussed.

Experimental Section

General Remarks. All manipulations were carried out in oxygen-free, rigorously dried solvents under high-purity argon. The NMR spectra were recorded with Bruker WH400, WM300, and WP80 spectrometers by using the standard procedures. ¹H NMR nuclear Overhauser spectra were recorded in the difference mode.¹¹ ¹H and ¹³C chemical shifts are reported as δ values with either Me₄Si or the solvent signal (δ (C₆D₅CHD₂) 2.08 and δ (C₆D₅CD₂) 20.4, respectively) as the internal standard. The ³¹P chemical shifts are presented as δ values and are referenced to external 85% H₃PO₄.

IR spectra were run on a Nicolet FT IR 7199 spectrometer. The mass spectra were obtained on an Atlas-CH5 spectrometer.

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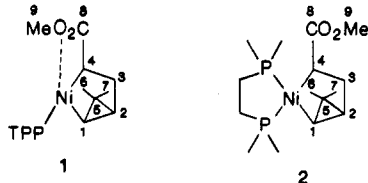
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Table I. ^{13}C NMR Data of 1 and 2 Dissolved in Toluene- d_8 at $T = 310\text{ K}$


		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
1 ^a	δ	18.87	38.45	28.44	52.81	19.17	23.54	28.85	184.81	51.09
	$^1J(\text{C,H})$, Hz (± 2)	150	156	125	131		122	125		146
	$J(\text{C,P})$, Hz (± 0.5)	26.5	14.1	3.1	51.5					
2 ^b	δ	38.39	38.16	34.35	51.86	20.94	23.81	30.66	183.28	49.21
	$^1J(\text{C,H})$, Hz	146	154	125	126		124	124		143
	$J(\text{C,P})$, Hz	34.1	2.5	5.1	61.6	2.2	2.5	2.1	5.8	
	$J(\text{C,P})$, Hz	81.9	13.2	11.8	7.6		2.5	3.1	1.2	

^a TPP signals for 1: C_{ipso} , δ 133.57 ($J(\text{P,C}) = 34\text{ Hz}$); C_{ortho} , δ 134.76 ($J(\text{C,H}) = 163.0$, $J(\text{C,P}) = 11.5\text{ Hz}$); C_{meta} , δ 128.19 ($J(\text{C,H}) = 161.5$, $J(\text{C,P}) = 9.0\text{ Hz}$); C_{para} , δ 129.52 ($J(\text{C,H}) = 161.5\text{ Hz}$). ^b dmpe signals: methylene carbons at δ 29.37 and 27.44 and methyl carbons at δ 13.50 (25.5, 2.1), 12.76 (23.5, 1.5), 12.14 (17.4, 0.7), and 10.15 (17.3, 0.7), $J(\text{P,C})$ in parentheses.

Melting points were determined with a Büchi SMP-20 apparatus in capillary tubes sealed under argon and are uncorrected. Microanalytical data for C, H, Ni, and P were provided by "Mikroanalytisches Laboratorium Dornis und Kolbe", D-4330 Mülheim a.d. Ruhr, West Germany.

Reagents. Published procedures were used to prepare Ni(cod)₂,¹² Ni(cdt),¹² bis(triphenylphosphane)nickel methyl acrylate,¹³ and 3,3-dimethylcyclopropene.¹⁴ Methyl acrylate (BASF) was distilled, triphenylphosphane (tpp; BASF) was recrystallized from diethyl ether, and both were stored under argon. Ethylenebis(dimethylphosphane) (dmpe) (Strem Chemicals, Inc.) was stored under argon without further purification.

Preparation of 4-(Triphenylphosphane)-2,2-dimethyl-5-(methoxycarbonyl)-4-nickelabicyclo[3.1.0]hexane (1). To an orange solution of (tpp)₂Ni(mac) (2.16 g, 3.23 mmol) in Et₂O (50 mL) was added at 0 °C a solution of dmcp (2.2 g, 3.23 mmol) in Et₂O (20 mL). A red solution was obtained that was stirred for 1 h at 0 °C. The solvent was evaporated under vacuum; the red oily residue was redissolved in Et₂O/hexane (20 mL, 1:2), filtered through a 3-cm Florisil pad, and cooled to -35 °C for 10 h. A solid was obtained that was separated by filtration, washed with cold hexane (3 × 10 mL), and dried under vacuum (10⁻³ torr) to yield orange crystals of 1: 0.95 g (65%); mp 133 °C dec; mass spectrum (70 eV), m/z (for ⁵⁸Ni) 474 (M⁺, relative intensity 1), 320 (2), 262 (27), 183 (22), 154 (100), 111 (61), 78 (40), 31 (44); IR (KBr) 1580 (C=O), 1296, 1259 cm⁻¹ (COC); ³¹P NMR (32 MHz, toluene-*d*₈, 20 °C) δ 26.3; for ¹H NMR and ¹³C NMR, see Tables I and II. Anal. Calcd for C₂₇H₂₉NiO₂P: C, 68.24; H, 6.15; Ni, 12.33; P, 6.52; mol weight (cryoscopic, benzene), 474. Found: C, 68.56; H, 6.36; Ni, 11.89; P, 5.99; mol wt, 485.

1 can also be prepared starting from Ni(cdt). To a red solution of Ni(cdt) (1.18 g, 5.36 mmol) in Et₂O (50 mL) was added at -50 °C mac (0.99 mL, 11 mmol). Then a solution of tpp (1.40 g, 5.36 mmol) in Et₂O was added dropwise whereby the color turned to yellow. This mixture was warmed to 0 °C, and at this temperature dmcp (0.5 mL, 5.36 mmol) in Et₂O (10 mL) was added. After workup as described above 1.88 g (74 %) of 1 was obtained.

Preparation of 4-[Ethylenebis(dimethylphosphane)]-2,2-dimethyl-5-(methoxycarbonyl)-4-nickelabicyclo[3.1.0]hexane (2). To a solution of (tpp)₂Ni(mac) (1.58 g, 2.36 mmol) in Et₂O (30 mL) was added at 0 °C a solution of dmcp (0.25 mL, 2.36 mmol) in Et₂O (10 mL). After the solution was stirred for 1 h at 0 °C, dmpe (0.35 g, 2.36 mmol) in Et₂O (10 mL) was added. The reaction mixture was warmed up to room temperature and stirred for another 1 h. The yellow solution was filtered through a 3-cm Celite pad and cooled to -78 °C. A solid was obtained that was separated by filtration at -78 °C and dried under vacuum

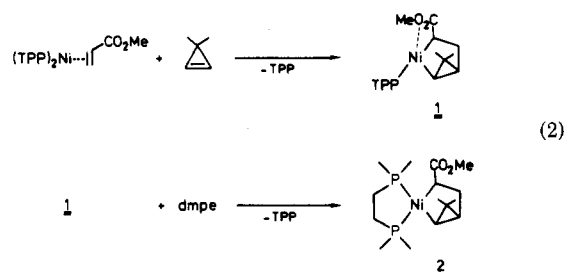
(10⁻³ torr) to yield yellow-orange crystals of 2: 0.85 g (99%); mp 109 °C; mass spectrum (70 eV), m/z (for ⁵⁸Ni) 362 (M⁺, relative intensity 1), 347 (14), 210 (28), 208 (94), 180 (100), 134 (39), 120 (25); IR (KBr) 1640 cm⁻¹ (C=O); ³¹P NMR (32 MHz, toluene-*d*₈, -50 °C) δ 37.7, and 27.6 ($J_{\text{pp}} = 3.1\text{ Hz}$); ¹H NMR and ¹³C NMR, see Tables I and II. Anal. Calcd for C₁₅H₃₀NiO₂P₂: C, 49.62; H, 8.33; Ni, 16.17; P, 17.06. Found: C, 49.83; H, 8.06; Ni, 16.20; P, 16.93.

Reaction of 1 with mac. 1 (0.43 g, 0.9 mmol) was dissolved in mac (5 mL) at 20 °C. After the solution was stirred for 2 h, mac was pumped off and the residue dissolved in Et₂O (10 mL). At -78 °C 0.38 g (88%) of crystalline 1 was recovered that was separated by filtration.

1 as Catalyst for the Cotrimmerization of dmcp with mac. 1 (0.17 g, 0.35 mmol) was dissolved in mac (20.5 g, 240 mmol), and dmcp (8.1 g, 120 mmol) was added to the yellow solution at ambient temperature. Immediately the temperature rose to 50 °C. The mixture had to be cooled by a water bath to keep the temperature at 40–45 °C. After completion of the addition of dmcp the temperature decreased. The mixture was heated to 40 °C for another 30 min and then distilled. One obtained mac [12.8 g; bp <30 °C (0.2 torr)] and a mixture of six cotrimers [15.1 g; bp 60–65 °C (0.2 torr)] with the composition (GC): 16.4% *trans*-3, 8.1% *cis*-3, 12.9% *trans*-4, 25.1% *cis*-4, 20.2% *trans*-5, 10.7% *cis*-5, and a total of 6.6% of four unknown compounds. The structures of 3–5 were confirmed by comparison of their GC retention times with those of authentic samples.¹⁰

Results and Discussion

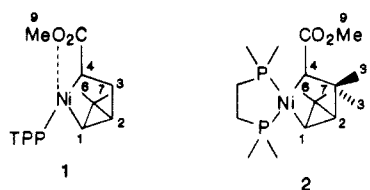
Treatment of (tpp)₂Ni(mac)¹³ with dmcp at 0 °C in Et₂O leads to displacement of one tpp ligand and the formation of 4-(triphenylphosphane)-*cis*-2,2-dimethyl-5-(methoxycarbonyl)-4-nickelabicyclo[3.1.0]hexane (1) in 65% yield. This compound can also be prepared starting from Ni(cdt), tpp, mac, and dmcp in the molar ratio of 1:1:2:1. In 1 the phosphorus ligand tpp can be easily displaced by the chelating diphosphane dmpe. Thereby 4-[ethylenebis(dimethylphosphane)]-*cis*-2,2-dimethyl-5-(methoxycarbonyl)-4-nickelabicyclo[3.1.0]hexane (2) is formed quantitatively (eq 2). Complexes 1 and 2 were charac-



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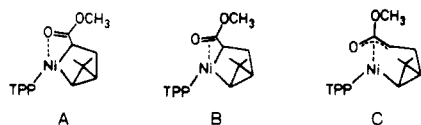
Table II. ^1H NMR Data of 1 and 2 Dissolved in Toluene- d_8 at $T = 300\text{ K}$ 

		H-1	H-2	H-3	H-3'	H-4	H-6	H-7	H-9
1 ^a	δ	-0.61	1.02	2.21	2.14	5.07	1.92	0.58	2.72
	$J(\text{H}_i, \text{H}_j)$, Hz	1,2, 7.3	2,3, 6.7 2,3', 2.8	3,3', 14.4		3,4, 8.1 3',4, 10.3			
	$J(\text{P}, \text{H})$, Hz	17.0	1.8	4.9		8.3			
	NOE enhancement ^b	2,7,4 TPP	1,7			3 TPP	9,7	1,2,6 TPP	
2 ^c	δ	+0.41	1.34	2.87	2.69	3.33	1.58	1.28	3.51
	$J(\text{H}_i, \text{H}_j)$, Hz	1,2, 7.8	2,3, 6.4 2,3', 2.7	3,3', 14.1		3,4, 7.7 3',4, 10.9			
	$J(\text{P}, \text{H})$, Hz	19.3	2.5	7.9	0.8	10.2			
	$J(\text{P}, \text{H})$, Hz	5.1	2.5	2.8	2.5	1.8			

^a TPP signals at δ 7.86 (ortho) and 7.10 (meta, para). ^b Observed at proton H_i , while proton H_j (on top of the corresponding column) was irradiated. ^c dmpe signals: methylene protons at δ 0.85 and 0.78 and methyl protons at δ 1.20, 1.08, 0.92, and 0.90.

terized by a combination of microanalytical data as well as by mass, IR, and NMR spectroscopy. The interpretation of the NMR data of 2 is straightforward. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2 exhibits an AX spectral pattern with $^3J(\text{P}_A, \text{P}_X) = 3.1\text{ Hz}$. Consequently the phosphorus couplings in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 2 can be obtained from first-order analysis. In the proton-decoupled ^{13}C NMR spectrum of 2 there are two signals for the two carbons that are σ -bonded to the metal. Each of these signals exhibits a larger and a smaller carbon-phosphorus coupling (cf. Table I). Therefore it can be assumed that the surrounding of Ni in 2 is approximately square-planar. All other carbon shifts and $J(\text{C}, \text{H})$ values support the metallacyclic structure of 2. The 400-MHz ^1H NMR spectrum of 2 is also in line with this interpretation. Moreover, from the vicinal $^3J(\text{H}, \text{H})$ couplings (cf. Table II) it can be deduced that exclusively that stereoisomer is present, in which the three-membered ring and the CO_2Me group are mutually cis. ($^3J(\text{H}_2, \text{H}_3)$ is small, indicating that these protons are nearly orthogonal. Furthermore $^3J(\text{H}_1, \text{H}_2)$ and $^3J(\text{H}_3, \text{H}_4)$ are around 7.7 Hz and $^3J(\text{H}_3, \text{H}_4)$ is 10.9 Hz, which is typical for an arrangement with a dihedral angle near 0 and 180°, respectively).

Structure elucidation for compound 1 is more difficult. Its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows only one singlet, and the ^1H and ^{13}C NMR spectra as well as microanalytical data confirm that the ratio of tpp, dmcp, and mac is 1:1:1. A molecular weight determination in benzene shows that compound 1 is monomeric in solution, and furthermore in the temperature range between -80 and +40 °C in the ^{13}C spectra there are no indications for the existence of more than one phosphorus ligand in the molecule. For a stable monomeric 16-electron Ni complex the following three limiting forms A, B, and C of 1 will be taken into account.



Significant contribution of the η^3 -oxaallyl structure C will be ruled out because the carbon shifts and $^1J(\text{C}, \text{H})$ couplings of C-1 and C-4 (cf. Table I) indicate that these carbon atoms are σ -bonded to Ni. (If an η^3 -oxaallyl moiety were present, we would expect for $J(\text{C}-4, \text{H})$ a value of more

than 140 Hz). The indications that the ester group might operate as an intramolecular donor are as follow: in 1 the CO stretching vibration is considerably shifted to a lower frequency (1580 cm^{-1}). Frequency shifts of the magnitude are known in the literature for metal complexes exhibiting bonding interactions between the methoxycarbonyl group and the metal.¹⁶⁻¹⁸ In the NMR spectra of 1 the largest chemical shift alterations (compared with those of 2) are observed for C-1 (probably transoid to the oxygen of the CO group), H-4, and the methoxy protons. Furthermore, the magnitudes of $^2J(\text{P}, \text{C}-4) = 51.5\text{ Hz}$ and $^2J(\text{P}, \text{C}-1) = 26.5\text{ Hz}$ support the suggestion that tpp is bonded transoid to C-4. All these observations are in agreement with a $\text{C}=\text{O}/\text{Ni}$ interaction but do not allow one to distinguish between a "side on" (B) or "end on" (A) complexation. Because complex B is more strained and $\delta(\text{C}-9)$ of 1 is very similar to that of 2, we consider form A to be more likely. Even at 400-MHz the ^1H NMR spectrum of 1 is complex; $J(\text{H}, \text{H})$ values (cf. Table II) were therefore extracted from spectrum simulation and iteration. From these data as well as from ^1H NMR NOE difference spectra (cf. Table II) it is concluded that the three-membered ring and the ester group are cis and that the conformation of this metallacycle is qualitatively similar to that in 2. (The argumentation with $^3J(\text{H}, \text{H})$ is similar as that above for 2. The NOE interactions of, e.g., H_1 with H_4 and H_3 with H_4 confirm that these protons are neighbored).

In summary, the molecular weight determination and the spectroscopic data suggest the metallacyclic structure A or B for compound 1. A strained metallacyclopentane like A or B is unprecedented in the literature. Complexes with η^3 -oxaallyl ligands have been synthesized but have not been isolated and characterized structurally.¹⁹ On the other hand, complexes with η^3 -allyl C_6 chains^{18,20} being

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isostructural to C as well as η^3 -1-azaallyl complexes²¹ are well-documented.

To the best of our knowledge compounds 1 and 2 are the first examples of nickelacyclopentanes formed by coupling of two different olefines at the metal. There are only two other stable mixed metallacyclopentanes, namely, 4-(cyclopentadienyl)-4-(triphenylphosphane)-2,2-dimethyl-5-nitrilo-4-cobaltabicyclo[3.1.0]hexane²² and a ferrabicyclo[3.2.0]heptane derivative²³ known to date whose role as possible intermediates in catalytic processes has not been investigated. We have obtained evidence that the

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nickel complex 1 can be regarded as an intermediate in the above-mentioned cotrimerization reaction of dmcp and mac (eq 1); for a proposed mechanism of this reaction see ref 10. Like the "in situ" catalyst obtained by mixing Ni(cod)₂ and tpp in the molar ratio of 1:1¹⁰ compound 1 catalyzes the cotrimerization at ambient temperature. Both types of catalysts produce almost identical yields and compositions of compounds 3-5. But we have also found that 1 does not react at all with dmcp or mac alone. This indicates that a mixture of both olefins is necessary to achieve a catalytic cycle. Further experiments are necessary in order to understand these phenomena.

Acknowledgment. We are grateful to Dr. D. Henneberg and Dr. K. Seevogel for providing mass and IR spectra, respectively.

Communications

Selectivity in C-O Bond Formation: Reaction of Acid Chlorides and Methyl Iodide with *trans*-MeOIr(CO)(PPh₃)₂

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Summary: Reactions of RX (RX = MeI, CH₃C(O)Cl, C₆H₅C(O)Cl, and C₆H₅CH₂C(O)Cl) with *trans*-MeOIr(CO)(PPh₃)₂ have been examined. In each case, an adduct is formed, RIr(OMe)(CO)(PPh₃)₂X, which is stable for R = Me. For the acid chlorides, this adduct eliminates ester, forming Ir(CO)(PPh₃)₂Cl. Thus the carbon-oxygen bond leading to ester products is formed more readily than the carbon-oxygen bond leading to dimethyl ether.

Transition-metal acyl complexes are key to two of the most important applications of homogeneous catalysts, hydroformylation and methanol carbonylation.¹⁻⁵ Acyl complexes may be formed by carbonylation of alkyl complexes (alkyl migration processes) or by addition of acid chlorides or aldehydes to 16-electron complexes.¹⁻³ The reactions thus far reported for acyl complexes appear to be limited to decarbonylation,⁶ reductive-elimination reactions (C-H, C-C, and C-I bond formation)^{5,7-10} and the

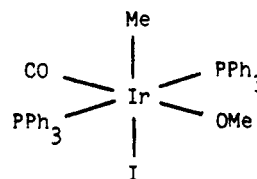
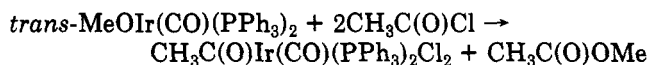


Figure 1. Suggested geometry for the MeI adduct with *trans*-MeOIr(CO)(PPh₃)₂. This geometry is consistent with the spectroscopic parameters.

recent report of β -elimination.¹¹ In order to expand the known reactions of acyl groups, we have begun to examine possible carbon-oxygen bond formation through oxidative addition of acid chlorides to the alkoxide complex, *trans*-MeOIr(CO)(PPh₃)₂.^{12,13} These reactions lead to C-O bond formation with production of esters. Carbon-oxygen bond formation has been previously reported on Ni(II) and Pd(II).¹⁴ Reaction with methyl iodide has also been examined as a comparison to the acid chlorides.

The reaction of acetyl chloride with *trans*-MeOIr(CO)(PPh₃)₂ leads to CH₃C(O)Ir(CO)(PPh₃)₂Cl₂ and CH₃C(O)OMe in high yield.¹⁵



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(15) A solution of 0.05 g of *trans*-MeOIr(CO)(PPh₃)₂¹³ in 5 mL of benzene was placed in a pressure tube fitted with a Teflon stopcock and brought out of the drybox. The tube was placed on a vacuum line and degassed, and 0.10 mL of purified acetyl chloride¹⁶ was distilled onto the solution. The solution was stirred for 1 h, after which the solvent was removed by vacuum distillation and saved for further analysis. The white solid CH₃C(O)Ir(Cl)₂(CO)(PPh₃)₂ (IR in KBr: 2060 (vs) and 1620 cm⁻¹ (s)¹⁷) and, depending upon the purity of the acetyl chloride used and the care of the workup, HIr(Cl)₂(CO)(PPh₃)₂ (IR in KBr: $\nu_{\text{C=O}}$ 2020 (vs) and $\nu_{\text{I-H}}$ 2238 (s) cm⁻¹) were formed. The distillate was analyzed for methyl acetate which was identified by IR and NMR (91% yield based on the Ir complex). Reactions of *trans*-MeOIr(CO)(PPh₃)₂ with phenylacetyl chloride and benzoyl chloride were done by Schlenk techniques and analyzed similarly.

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