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Reaction of Organolithium Reagents with Cyclorhenated and Cyclomanganated (η^6-Arene)tricarbonylchromium Complexes: Structural Characterization of a New Benzoylrhenate Intermediate and Selective Ortho-Acetylation of (η^6-Arene)tricarbonylchromium Complexes

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The nucleophilic addition of PhLi to tetracarbonyl[3-methyl-2-{(η^6-phenyl)tricarbonylchromium(0)}pyridine]rhenium(I) yields the air-stable (*exo*-benzoyl)(tricarbonyl)[3-methyl-2-{(η^6-phenyl)tricarbonylchromium(0)-$\kappa C^{2'}$}pyridine-κN]rhenate(I) that has been isolated and characterized by X-ray diffraction analysis and other spectroscopic methods. A similar treatment applied to cyclomanganated (η^6-arene)$Cr(CO)_3$ analogues with a nucleophile such as MeLi provides a new route to the synthesis of ortho disubstituted (η^6-acetophenone)$Cr(CO)_3$ derivatives.

Introduction

We recently reported that the reaction of organolithium reagents with cyclomanganated aromatic ligands, of the formula *cis*-LL′$Mn(CO)_4$, could lead to reactive acylmanganate intermediates that convert either into new aromatic ketones after a reductive-elimination process or into a new class of (η^3-benzyl)tricarbonylmanganese complexes upon alkylation.[1] We showed also that the nucleophilic attack of RLi at a *cis*-LL′$Re(CO)_4$ (LL′= 2-phenylpyridine) complex takes place at one of the two axial carbonyl ligands,[2] this being in good agreement with the theoretical prediction made for the reactivity of $LM(CO)_5$ complexes versus nucleophiles.[3]

We therefore extended our explorations to cyclomanganated (arene)tricarbonylchromium complexes,[4] which led to the synthesis of a new class of syn-facial heterobimetallic (Cr, Mn) cyclohexadienylbenzylidene complexes that resulted from the successive treatment of the bimetallic substrates with PhLi and MeOTf.[5,6] The molecular structures of the products led us to suggest that the regioselective addition of the organolithium reagent took place at the less hindered axial CO ligand, e.g. the one located exo with respect to the $Cr(CO)_3$ fragment (Scheme 1).

Herein, we confirm the latter assumption as we now present the molecular structure of a benzoylrhenate species derived from the reaction of PhLi with tetracarbonyl[3-methyl-2-{(η^6-phenyl)tricarbonylchromium(0)-$\kappa C^{2'}$}pyridine-κN]rhenium(I). We also propose that the degradation of acylmanganate species by reductive elimination to give aromatic ketones is a valuable new synthetic method for the regioselective ortho-acetylation of (η^6-arene)tricarbonylchromium complexes.

Results and Discussion

Synthesis and Structural Characterization of the Benzoylrhenate Species. The synthesis of the

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(6) List of the abbreviations used throughout this article: DME, 1,2-dimethoxyethane; THF, tetrahydrofuran; MeOTf, methyl triflate or methyl trifluoromethanesulfonate; PPN, bis(triphenylphosphoranylidene)ammonium; PhLi, phenyllithium; MeLi, methyllithium.

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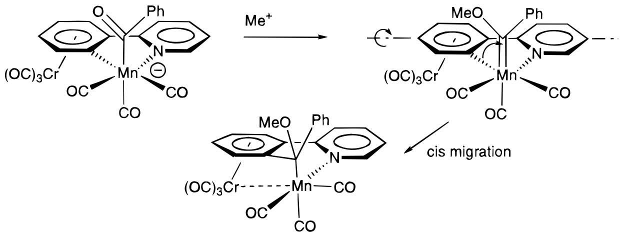
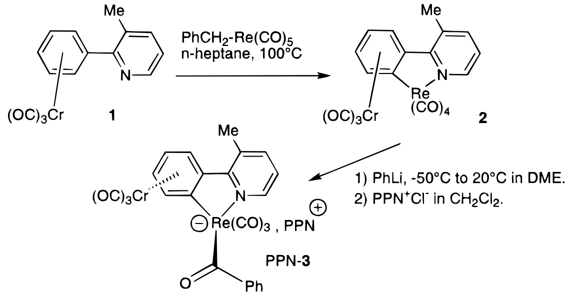
Scheme 1



Scheme 2



bimetallic complex **2** from 3-methyl-2-{(η^6-phenyl)tricarbonylchromium(0)}pyridine, complex **1**, was done by applying the common procedure described for analogous cyclometalation reactions that involve a thermolytic treatment of the aromatic substrate with $R{-}M(CO)_5$ (R− = Me−, M = Re; R− = Me−, $PhCH_2$−, M = Mn) complexes.[7] Noteworthy, a cyclorhenation of benzo[*h*]quinoline by $Re(CO)_5Cl$ has also been reported.[8] Instead of using $Me{-}Re(CO)_5$[9] we preferred $PhCH_2{-}Re(CO)_5$,[10] which could be readily synthesized by reaction of a stoichiometric mixture of sodium pentacarbonylrhenate and benzyl chloride in dry THF. The resulting product could be purified by chromatography on silica gel and isolated as a colorless oil at room temperature.

After reflux overnight of a mixture of **1** and $PhCH_2{-}Re(CO)_5$ in *n*-heptane and subsequent chromatographic purification, complex **2** was obtained with an optimum yield of 69% (Scheme 2).

The reaction of complex **2** with a slight excess of PhLi at −50 °C in 1,2-dimethoxyethane yielded quantitatively the corresponding lithium (benzoyl)(tricarbonyl)[3-methyl-2-{(η^6-phenyl)tricarbonylchromium(0)-$\kappa C^{2'}$}-pyridine-κN]rhenate(I), complex Li-**3**.[11] The latter salt was immediately submitted to metathesis of Li^+ for the bulkier PPN^+ countercation in the presence of a stoichiometric amount of PPN^+Cl^- in CH_2Cl_2 (Scheme 1). The resulting salt, PPN-**3**, was crystallized from a mixture of CH_2Cl_2 and hexane and afforded crystals suitable for an X-ray diffraction analysis. Acquisition and refinement data are listed in Table 1. Selected interatomic distances, angles, and torsion angles are gathered in Table 2. Figure 1 displays an ORTEP view of the molecular structure of the anionic fragment of PPN-**3**. This picture indicates clearly that the nucleophile PhLi has added to the less sterically hindered axial carbonyl ligand of the $Re(CO)_4$ fragment, opposite to the $Cr(CO)_3$ group (Figure 1).

Table 1. Crystallographic Data and Summary of Data Collection and Refinement for PPN-3

formula	$[C_{25}H_{15}NO_7CrRe]^-[C_{36}H_{30}NP_2]^+\cdot CH_2Cl_2$
dimens, mm	0.15 × 0.20 × 0.25
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	9.7434(3)
b, Å	17.2076(3)
c, Å	18.9084(4)
α, deg	116.849(2)
β, deg	101.456(2)
γ, deg	91.250(2)
V, Å^3	2749.5(1)
Z	2
ρ_{calc}, g cm^{-3}	1.57
μ, mm^{-1}	2.61
F(000)	1304
diffractometer	Nonius KappaCCD
radiation	Mo Kα
λ, Å	0.710 73
T, K	123(2)
max 2*θ*, deg	56.6
no. of data	40511
no. of unique data	12 752 (R_{int} = 0.041)
no. of unique data [$I > 2\sigma(I)$]	10 493
no. of variables	695
R(*F*) [for $I > 2\sigma(I)$]	0.026
w$R_2(F^2)$ [for all data]	0.052
S	0.99
largest diff peak and hole, e/Å^3	1.43/−0.99

The overall structure of **3** possesses geometric characteristics similar to those of the (acetyl)(tricarbonyl)-[2-(phenyl-$\kappa C^{2'}$)pyridine-κN]rhenate(I), PPN-**4**, an analogue described previously by us[2] (Figure 2).

A slight shift from coplanarity is noticed for the two aromatic rings of the chelating ligand and can be quantified in terms of a value of 6.3° for the torsion angle N(1)−C(6)−C(7)−C(8). The shortest rhenium−carbonyl carbon bond is observed for Re(1)−C(1RE) (1.912(3) Å) which is trans to the *σ*-donor pyridyl fragment. The two other Re(1)−C(2RE) and Re(1)−C(3RE) bond distances are significantly longer (about 1.95 Å). The electron-withdrawing effect of the $Cr(CO)_3$ moiety can be evaluated by comparison with the structural values obtained for PPN-**4**. Indeed, in complex PPN-**3** the carbon−rhenium bond distance Re(1)−C(8) is shorter than in PPN-**4** by an approximate value of 0.1 Å suggesting an increased back-donation to the conjugated aromatic system.

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(11) The systematic nomenclature for octahedral coordination systems can be applied to anion **3** in order to explicit the position of the benzoyl group. Therefore, the nitrogen atom of the pyridine ligand has priority number 1, the ipso aromatic carbon bound to Cr and to the Re center has priority number 2, the CO ligands have priority number 3, and the PhC(O)− group has priority number 4. Therefore, we propose for **3** the following: *fac*- or (OC-6−33)-(*exo*-benzoyl)(tricarbonyl)[(3-methyl-2-{(η^6-phenyl)tricarbonylchromium(0)−$\kappa C^{2'}$})pyridine−κN]rhenate(I). For anion **4** we propose the following: *fac*- or (OC-6-22)-(acetyl)(tricarbonyl)[2-(phenyl-$\kappa C^{2'}$)pyridine-κN]rhenate(I). For leading references, see: Leigh, G. J., Ed. *IUPAC Nomenclature of Inorganic Chemistry, Recommendations 1990*; Blackwell Scientific Publication: Oxford, 1991; pp 143−206.

Table 2. Selected Interatomic Bond Distances, Angles, and Torsion Angles for PPN-3·CH_2Cl_2

Selected Interatomic Distances (Å)			
Re(1)−C(1RE)	1.912(3)	Cr(1)−C(10)	2.214(2)
Re(1)−C(3RE)	1.951(3)	Cr(1)−C(11)	2.234(2)
Re(1)−C(2RE)	1.953(2)	Cr(1)−C(12)	2.248(2)
Re(1)−C(8)	2.140(2)	Cr(1)−C(7)	2.262(2)
Re(1)−N(1)	2.1752(19)	Cr(1)−C(8)	2.326(2)
Re(1)−C(13)	2.192(2)	C(13)−C(14)	1.513(3)
Cr(1)−C(9)	2.212(2)	C(13)−O(13)	1.235(2)
Selected Interatomic Bond Angles (deg)			
C(1RE)−Re(1)−C(3RE)	91.79(10)	C(3RE)−Re(1)−C(13)	172.75(9)
C(1RE)−Re(1)−C(2RE)	92.30(10)	C(2RE)−Re(1)−C(13)	94.10(9)
C(3RE)−Re(1)−C(2RE)	91.13(9)	C(8)−Re(1)−C(13)	81.82(8)
C(1RE)−Re(1)−C(8)	94.82(9)	N(1)−Re(1)−C(13)	82.55(8)
C(3RE)−Re(1)−C(8)	92.36(8)	C(2CR)−Cr(1)−C(1CR)	88.36(11)
C(3RE)−Re(1)−N(1)	91.83(8)	C(2CR)−Cr(1)−C(3CR)	87.02(10)
C(2RE)−Re(1)−N(1)	97.17(9)	C(1CR)−Cr(1)−C(3CR)	90.07(11)
C(8)−Re(1)−N(1)	75.49(8)	C(2CR)−Cr(1)−C(9)	88.00(9)
Selected Torsion Angles (deg)			
C(1RE)-Re(1)−C(8)−C(9)	2.92(19)	C(8)−Re(1)−C(13)−O(13)	49.56(18)
N(1)−C(6)−C(7)−C(8)	6.3(3)		

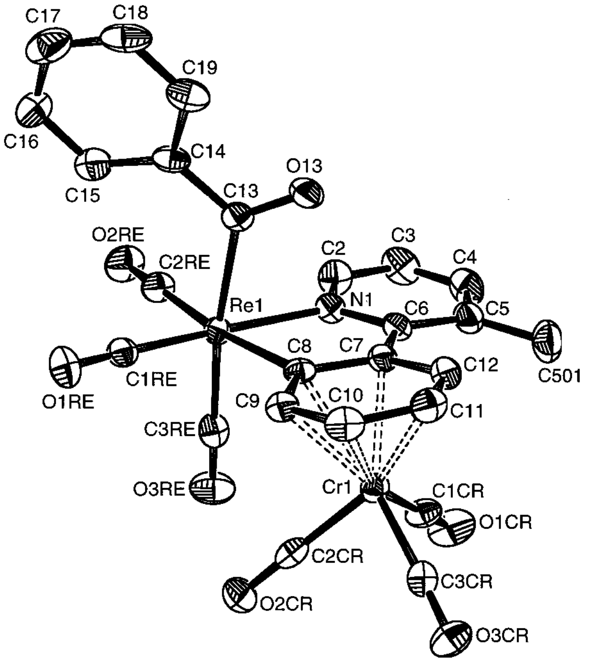


Figure 1. ORTEP view of PPN-**3**. PPN^+ and CH_2Cl_2 as well as hydrogen atoms have been omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

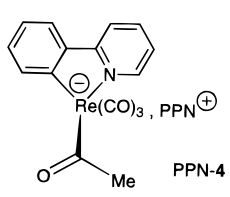
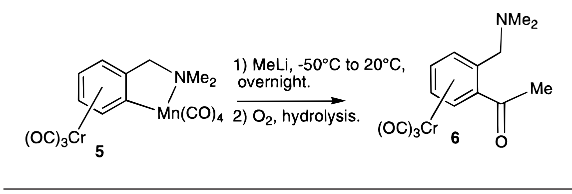


Figure 2. Bis(triphenylphosphoranylidene)ammonium *fac*-(acetyl)(tricarbonyl)[2-(phenyl-*κC*$^{2'}$),pyridine-*κN*]rhenate-(I), PPN-**4**.

The bulkyness of the benzoyl(tricarbonyl)rhenium moiety forces the $Cr(CO)_3$ tripod to slightly shift from the symmetric central coordination position as indicated by the particularly long Cr(1)−C(8) and Cr(1)−C(7) bond distances of 2.326(2) and 2.262(2) Å, respectively. A slight folding of the coordinated aromatic ring can also be noticed. The interplanar angle of 5.0° formed between the least-squares planes C(7)−C(12)−C(11)−C(10)−C(9) and C(7)−C(8)−C(9) exceeds that reported for $[Et_4N]^+$-$[(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]^-$.[12a,b] The significant structural distortions observed for PPN-**3** are supposed to reflect steric effects arising from the chelation of the PhC(O)−$Re(CO)_3$ fragment which reduces the conformational flexibility of the bimetallic skeleton. Therefore, it can less readily minimize steric contacts with the Cr-$(CO)_3$ rotor by a rotation around the Re(1)−C(8) axis as it is the case for the $(CO)_5W$ fragment in $[Et_4N]^+$-$[(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]^-$.[12a] The torsion angle C(1RE)−Re(1)−C(8)−C(9) has a value of only 2.92(19)° in PPN-**3** while it amounts to 15.1° for the above-mentioned anionic isoelectronic bimetallic (Cr, W) analogue.[12a] In other terms, this suggests that when no other option is available for the minimization the steric interaction between the $Cr(CO)_3$ tripod and a bulky aromatic substituent, the molecule may concede a slight folding of the complexed aromatic ring.

With respect to the value obtained for **2**, the IR spectrum of PPN-**3** in CH_2Cl_2 indicates a 23 cm^{-1} shift to lower frequencies of the E vibration mode of $Cr(CO)_3$ that confirms a significant transfer of electron density to the chromium center.

Ortho-Acetylation of (η^6-Arene)tricarbonylchromium Complexes. Recently,[1] we reported that the acylmanganate species were prone to decomposition by a reductive elimination process yielding eventually a new aromatic ketone coordinated to an electron deficient $Mn(CO)_3^-$ species. This process was fast in the case of cyclomanganated 2-phenylpyridine derivatives and was generally observed when the acylmetalate was allowed to warm above 0 °C. The addition of MeLi to cyclomanganated (η^6-arene)tricarbonylchromium complexes leads to acetylmanganates that require long reaction times to evolve toward the formation of derivatives of acetophenone. For instance, complex **5**[4a] was selectively converted within about 15 h into **6** with 68% yield (eq 1).

 (1)

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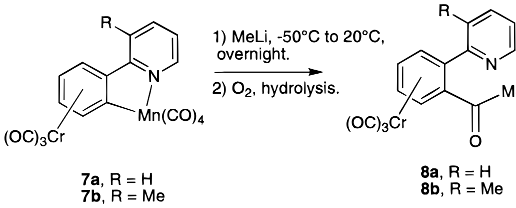
Similarly, the pyridine derivatives **7a**,**b**[4b] were converted into the corresponding acetyl substituted complexes **8a**,**b** with yields of 62% and 57%, respectively (eq 2). In all cases, the manganese center underwent oxidation to give untractable products after aerobic workup of the reaction medium.



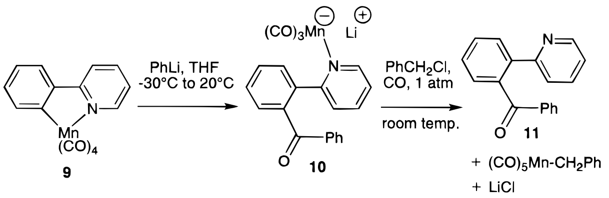
(2)

The reactions shown here indicate that the degradation of the acylmanganate species can be exploited in a novel synthetic methodology for regioselective ortho-acetylation of (η^6-arene)tricarbonylchromium complexes bearing at least one endogenous ligand such as $-CH_2-NR_2$ or pyridine. The method described herein is a reasonable alternative to the indirect introduction of the acetyl group either by applying the "umpolung" principle[13] through the introduction of an "acetyl anion"[14] equivalent by S_NAr processes[15] involving 2-lithio-2-methyldithiane or the cyanohydrin derivatives $Li-C(CN)(OR)(CH_3)$ as nucleophiles or by applying the classical Friedel−Craft Lewis-acid-catalyzed acetylation method to (η^6-arene)$Cr(CO)_3$ complexes.[16] Noteworthy also is the $Ru_3(CO)_{12}$-catalyzed carbonylation of 2-phenylpyridine by C−H bond activation at high pressure of CO and olefin developped by Murai and co-workers.[17]

After completion of the reductive-elimination process, the low-valent manganese carbonyl fragment can be recycled to give $PhCH_2-Mn(CO)_5$ when the reaction is performed under a 1 atm pressure of CO in the presence of benzyl chloride. An attempt to recover $PhCH_2-Mn(CO)_5$ was thus carried out subsequently to a reaction of complex **9** with 1 equiv of PhLi at −30 °C in THF (Scheme 3). The solution was slowly warmed to room temperature within 1 h, and 1 equiv of benzyl chloride was added under a gentle stream of CO. After purification by chromatography on silica gel ketone **11**[1] and $PhCH_2-Mn(CO)_5$ were isolated with 64% and 33% yield, respectively.

Conclusion. The molecular structure of a rhenium analogue of the benzoylmetalate presumably formed upon addition of PhLi to cyclomanganated (η^6-arene)tricarbonylchromium complexes established the predominant stereocontrol provided by the $Cr(CO)_3$ moiety and confirmed the preference of the organolithium reagent for the axial carbonyl ligand of the $Mn(CO)_4$ and $Re(CO)_4$ fragments. The degradation of the acetylmanganate species could be applied to a novel synthetic route to (η^6-acetophenone)tricarbonylchromium derivatives. Further applications of cyclometalated (η^6-arene)-$Cr(CO)_3$ complexes to metal-mediated synthesis are under current investigation.

Scheme 3



Experimental Section

General Comments. All reactions and workup procedures were carried out under a dry argon atmosphere. Products were isolated and purified by flash chromatography using deactivated silica gel (60 μm). ^{1}H and ^{13}C NMR spectra were acquired on Bruker WR 250, AC 300, AC 400, and DRX 500 equipment. Infrared spectra were performed on a FT-IR Nicolet Magna 550 spectrometer. Mass spectra and high-resolution mass determination were performed at the Analytical Center of the Chemical Institutes of the University of Bonn by using the electron impact method. Elemental analyses (reported in % mass) were performed at the Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, Bonn, Germany, and at the Faculté de Chimie de l'Université Louis Pasteur, Strasbourg, France.

Synthesis of $PhCH_2-Re(CO)_5$. To a suspension of Na (1 g, 0.0435 mol)/Hg (5 mL) amalgam in THF (50 mL) at 0 °C was added $Re_2(CO)_{10}$ (5 g, 0.0153 mol of Re). The mixture was stirred for 1.5 h and the reddish solution transferred via a cannula to a new vessel in which was placed a stoichiometric amount of $PhCH_2-Cl$ (1.938 g, 0.0153 mol). The reaction mixture was warmed to room temperature and stirred for 2.5 h. The resulting pale yellow suspension was then brought to reflux for 15 min, cooled to room temperature, and added to silica gel, and the solvent was removed in vacuo. The coated silica gel was placed on the top of a packed SiO_2 column, and $PhCH_2-Re(CO)_5$ was eluted with *n*-hexane. The pure compound was recovered after removal of the solvents in vacuo with 88% yield (5.65 g). IR (CH_2Cl_2) [ν(CO)]: 2127.2 (w), 2014.1 (vs) 1980.6 (s) cm^{-1}. MS (EI) (*m*/*e*): 417.9 (M)$^+$, 389.9 (M − CO)$^+$, 362.0 (M − 2CO)$^+$, 334.0 (M − 3CO)$^+$, 306.0 (M − 4CO)$^+$, 276.0 (M − 5CO)$^+$, 250.0, 91.1 (M − Re − 5CO)$^+$. High-resolution MS (IE): calcd for $C_{12}H_7O_5Re$, 417.9823; found (intensity, %), 417.9854 (34.67).

Synthesis of Tetracarbonyl[3-methyl-2-{(η^6-phenyl)-tricarbonylchromium (0)-$\kappa C^{2'}$}pyridine-κN]rhenium(I), 2. To a solution of complex **1** (600 mg, 1.97 mmol) in *n*-heptane (20 mL) was added $PhCH_2-Re(CO)_5$ (821 mg, 1.97 mmol). The mixture was brought to reflux and stirred for 24 h. The reaction medium was cooled to room temperature, the solvent evaporated under reduced pressure, and the raw product purified by column chromatography on silica gel. The orange band containing complex **2** was eluted with a mixture of CH_2Cl_2/hexane (1:1), and the solid compound was isolated after removal of the solvents under reduced pressure (820 mg, 69% yield). IR (CH_2Cl_2) [ν(CO)]: 2096.5 (w), 2000.1 (vs), 1978.9 (m), 1953.8 (s), 1934.5 (s), 1880.5 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.86 (d, 1H), 7.76 (d, 1H), 7.17 (t, 1H), 6.09 (m, 2H), 5.54 (t, 1H), 5.38 (t, 1H), 2.78 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$): δ 23.2 (py−CH_3), 92.8, 93.2, 94.0, 107.8, 114.6, 123.8, 125.4, 134.4, 143.7, 153.3, 164.9, 185.5 (Re−CO), 186.5 (Re−CO), 190.3 (Re−CO), 191.8 (Re−CO), 235.0 (Cr−CO) ppm. MS (EI) (*m*/*e*): 603.0 (M)$^+$, 547.1 (M − 2CO)$^+$, 519.0 (M − 3CO)$^+$, 491.1 (M − 4CO)$^+$, 463.1 (M − 5CO)$^+$, 435 (M − 6CO)$^+$, 405, 353, 221, 168. High-

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resolution MS (EI): calcd for $C_{19}H_{10}NO_7CrRe$, 602.9392; found (intensity, %): 602.9419 (3.41). Anal. Calcd for $C_{19}H_{10}O_7NCrRe$: C, 37.88; H, 1.67; N, 2.32. Found: C, 37.89; H, 1.68; N, 2.19.

Synthesis of Bis(triphenylphosphoranylidene)ammonium (*exo*-Benzoyl)(tricarbonyl)[3-methyl-2-{(η^6-phenyl)tricarbonylchromium(0)-$\kappa C^{2'}$}pyridine-κN]rhenate(I), PPN-3. To a solution of complex **2** (300 mg, 0.497 mmol) in 1,2-dimethoxyethane at −50 °C was added dropwise a slight excess of a solution of PhLi in hexane (1.8 M, 0.3 mL, 0.54 mmol). The resulting orange-red mixture was kept at −50 °C for 30 min and warmed slowly to room temperature, and the solvent was removed under reduced pressure. The dark orange residue was washed twice with dry pentane and added with PPN^+Cl^-, and the mixture was dissolved in 10 mL of dry CH_2Cl_2. The solution was stirred 30 min, combined with a few drops of dry diethyl ether, and filtered through a plug of Celite. The solution was concentrated to ca. 1 mL and added to a large volume of *n*-hexane. The resulting orange-yellow crystals, PPN-**3**, were then recrystallized twice from a mixture of CH_2Cl_2 and pentane (403.2 mg, 67%). IR (CH_2Cl_2): ν(CO), 1981 (s), 1939 (s), 1884 (sh), 1857 (vs) cm^{-1}; ν (C(O)−Ph), 1589 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.73 (s, 3H, CH_3−py), 5.12 (m, 2H), 6.10 (m, 1H), 6.25 (m, 1H), 6.81 (t, 1H, $^3J = 7.2$ Hz), 7.07 (t, 1H, $^3J = 6.7$ Hz), 7.14 (m, 2H), 7.44−7.62 (m, 28 H), 8.89 (d, 1H, $^3J = 5.2$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 23.1 (CH_3−py), 83.7, 94.6, 96.9, 105.9, 115.2, 121.7, 126.4 (d, $J = 106$ Hz, PPN^+), 126.5, 127.3, 129.6 (m, PPN^+), 132.0 (m, PPN^+), 133.9, 140.5, 152.0, 155.3, 155.8, 163.6, 198.9 (Re−*C*O), 204.2 (Re−*C*O), 206.7 (Re−*C*O), 237.0 (Cr−*C*O), 277.4 (s, Re−*C*(O)−Ph) ppm. Anal. Calcd for $C_{61}H_{45}O_7N_2P_2CrRe$: C, 60.14; H, 3.72; N, 2.30. Found: C, 59.58; H, 3.67; N, 2.14.

Procedure for the Structure Determination of PPN-3. PPN-**3** was crystallized from a mixture of hexane and CH_2Cl_2 to afford an orange-yellow single crystal that was submitted to X-ray diffraction analysis. The molecular structure of PPN-**3** was solved by direct methods (SHELXTL-Plus).[18] The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-93).[19] H atoms were refined using a riding model. An empirical absorption correction was applied (minimum/maximum transmission 0.5633/0.6233). Further details of data collection and refinement are given in Table 1. PPN-**3** crystallized with one molecule of CH_2Cl_2 per unit cell.

General Procedure for the Metal-Mediated Acetylation of [η^6-(Arene)]tricarbonylchromium. To a solution of the starting bimetallic complex in dry DME was added MeLi (1.2 equiv) at −50 °C. The temperature of the reaction mixture was slowly raised to room temperature during 3 or 4 h. The color of the mixture changed from bright orange to deep red-brown. The reaction mixture was stirred overnight and the vessel eventually opened to air. The brownish suspension that formed rapidly was filtered through a plug of Celite. The resulting solution was mixed with silica gel and the solvent removed under reduced pressure. The resulting coated silica gel was loaded on the top of a silica gel column that was packed in hexane.

[η^6-(2-acetyl-*N*,*N*-Dimethyl-2-acetylbenzylamine)]tricarbonylchromium, 6. Compound **5** (220 mg, 0.50 mmol), MeLi (0.37 mL, 0.6 mmol), and DME (15 mL) were combined with chromatography on SiO_2 [diethyl ether/methanol (90:10)], resulting in a 68% yield (107 mg) of complex **6**. IR (CH_2Cl_2): ν(CO), 1975 (s), 1900 (s), 1687 (m). ^1H NMR (C_6D_6): δ 4.92 (m, 2H), 4.67 (t, 1H, $J = 6.0$ Hz), 4.21 (t, 1H, $J = 6.0$ Hz), 3.90 (d, 1H, $J = 15.0$ Hz), 2.91 (d, 1H, $J = 15.0$ Hz), 2.01 (s, 3H), 1.96 (s, 6H) ppm. ^{13}C NMR (C_6D_6): δ 232.03 ($Cr(CO)_3$), 196.87 ($C(O)CH_3$), 112.15 (C_{Ar}), 101.38 (C_{Ar}), 95.07 (C_{Ar}), 94.29 (C_{Ar}), 91.41 (C_{Ar}), 88.63 (C_{Ar}), 60.29 ($PhCH_2NMe_2$), 45.28 (NMe_2), 28.37 (Me) ppm. MS (FAB^+) (*m*/*e*): 313.9 $(MH)^+$, 285.9 $(MH - CO)^+$, 256.9 $(M - 2CO)^+$, 228.9 $(M - 3CO)^+$, 214.9 $(MH - 3CO - Me)^+$. MS (EI) (*m*/*e*): 313.3 $(M)^+$, 284.6 $(M - CO)^+$, 256.6 $(M - 2CO)^+$, 228.5 $(M - 3CO)^+$, 185.4 $(M - 3CO - Me - CO)^+$, 128 $(M - 3CO - Me - CO{-}CH_2NMe_2)^+$. High-resolution MS ($FAB^+$): calcd for $C_{14}H_{16}NO_4Cr$ (MH^+), 314.048 455; found, 314.048 561.

[η^6-{(2-(2′-Acetyl)phenylpyridine}]tricarbonylchromium, 8a. Compound **7a** (200 mg, 0.44 mmol), MeLi (0.33 mL, 0.53 mmol), and DME (15 mL) were combined with chromatography on SiO_2 [diethyl ether/methanol (99:1)], resulting in a 62% yield (90 mg) of complex **8a**. IR (CH_2Cl_2): ν (CO), 1977 (s), 1907 (s), 1690 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.61 (d, 1H, $J = 4.8$ Hz), 7.87 (td, 1H, $J^3 = 7.9$ Hz, $J^4 = 1.8$ Hz), 7.66 (d, 1H, $J^3 = 8.0$ Hz), 7.37 (ddd, 1H, $J^3 = 7.6$ Hz, $J^3 = 4.8$ Hz, $J^4 = 1.0$ Hz), 5.80 (dd, 1H, $J^3 = 6.5$ Hz, $J^4 = 1.0$ Hz), 5.74 (td, 1H, $J^3 = 6.3$ Hz, $J^4 = 1.0$ Hz), 5.66 (dd, 1H, $J^3 = 6.5$ Hz, $J^4 = 1.0$ Hz), 5.44 (td, 1H, $J^3 = 6.3$ Hz, $J^4 = 1.0$ Hz), 2.18 (s, 3H) ppm. ^{13}C NMR (CD_2Cl_2): δ 232.15 ($Cr(CO)_3$), 199.30 ($C(O)CH_3$), 154.50 (C_{Ar}), 149.35 137.5, 124.2, 123.3, 110.7 (C_{ArCr}), 107.7 (C_{ArCr}), 94.1 (C_{ArCr}), 94.0 (C_{ArCr}), 92.1 (C_{ArCr}), 90.0 (C_{ArCr}), 30.7 (CH_3−C(O)−) ppm. Anal. Calcd for $C_{16}H_{11}O_4NCr$: C, 57.66; H, 3.33; N, 4.20. Found: C, 57.55; H, 3.36; N, 4.08.

[η^6-{2-[(2′-Acetyl)phenyl]-3-methylpyridine}]tricarbonylchromium, 8b. Compound **7b** (180 mg, 0.38 mmol), MeLi (0.29 mL, 0.46 mmol), and DME (15 mL) were combined with chromatography on SiO_2 [diethyl ether/methanol (95:5)], resulting in a 57% yield (75 mg) of air-stable crystalline orange complex **8b**. IR (CH_2Cl_2): ν(CO), 1977 (s), 1909 (s), 1686 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.50 (d, 1H, $J^3 = 4.7$ Hz), 7.53 (d, 1H, $J^3 = 7.6$ Hz), 7.22 (dd, 1H, $J^3 = 7.6$ Hz, $J^3 = 4.7$ Hz), 5.87 (d, 1H, $J^3 = 6.5$ Hz), 5.63 (t, 1H, $J^3 = 6.4$ Hz), 5.33 (m, 2H), 2.25 (s, 3H), 2.02 (s, 3H) ppm. ^{13}C NMR (CD_2Cl_2): δ 232.0 ($Cr(CO)_3$), 197.9 (−$C(O)CH_3$), 153.8, 147.2, 138.4, 132.5, 123.8, 115.2 (C_{ArCr}), 103.5 (C_{ArCr}), 94.2 (C_{ArCr}), 92.9 (C_{ArCr}), 92.65 (C_{ArCr}), 90.4 (C_{ArCr}), 28.8 ($CH_3C(O)$−), 19.54 (CH_3−py) ppm. Anal. Calcd for $C_{17}H_{13}O_4NCr$: C, 58.79; H, 3.77; N, 4.03. Found: C, 58.47; H, 3.60; N, 3.93.

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Supporting Information Available: Listings of crystallographic data (17 pages) and the corresponding crystallographic information file (CIF) for the structure reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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