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Reaction of Organolithium Reagents with Tetracarbonyl[2-(phenyl-$\kappa C^{2'}$),pyridine-κN]rhenium(I): Isolation and Structural Characterization of Acyl Rhenate Species

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Introduction

The chemistry of cyclomanganated and -rhenated complexes has developed rapidly in the past two decades.[1] Many examples of aromatic substrates are known to undergo a cyclometalation reaction when reacted with alkylpentacarbonylmanganese or -rhenium complexes under thermal conditions.[2] Cyclomanganated aromatics display a smaller spectrum of reactivity than other families of cyclometalated arenes.[3] Indeed, most of the reactions reported to take place with cyclomanganated complexes deal with photochemically or thermally promoted insertion reactions of unsaturated hydrocarbons or inorganic molecules.[4] Recently, we focused on the reactivity of organolithium reagents toward tetracarbonyl[2-(phenyl-$\kappa C^{2'}$),pyridine-κN]manganese(I) derivatives and demonstrated that a nucleophilic attack of aryllithium reagents yields novel acyl(tricarbonyl)manganate anions that have been characterized by ^{13}C NMR spectroscopy.[5] The detailed molecular structure of these anions could not be established due to their high sensitivity to air and their propensity to decomposition at ambient temperature. We reported that upon alkylation these anionic acyl manganese complexes afford a novel type of (tricarbonyl)manganese η^3-benzyl complexes. Now we turn our attention to the rhenium cyclometalated analogues presuming that the anionic intermediates resulting from the nucleophilic addition of organolithium reagents are expected to be more stable in the rhenium case, which might allow a thorough structural characterization of these anionic acylrhenium complexes. In this note we present our results on the reactivity of tetracarbonyl[2-(phenyl-$\kappa C^{2'}$),pyridine-κN]rhenium(I),[6] **1**, toward phenyllithium and methyllithium, and we report on the unprecedented isolation and characterization of two different (acyl)(tricarbonyl)[2-(phenyl-$\kappa C^{2'}$),pyridine-κN]rhenate(I) species, PPN-**2a** and PPN-**2b**. We further present the molecular structure of complex PPN-**2b** resulting from the addition of methyllithium to **1**.

Experimental Section

Synthesis of the Rhenium Acylates PPN-2a and PPN-2b. A typical procedure for the synthesis of PPN-**2a** and PPN-**2b** is as follows. To a solution of tetracarbonyl[2-(phenyl-$\kappa C^{2'}$),pyridine-κN]rhenium(I) in diethyl ether (15 mL) was added a solution of organolithium reagent in diethyl ether (1 equiv) under a dry atmosphere of argon at −78 °C. The yellow solution was slowly warmed to −30 °C and stirred for 1 h. The resulting orange mixture was evaporated under reduced pressure, and the residue was washed with dry hexane. The orange solid was combined with 1 equiv of bis(triphenylphosphoranylidene)ammonium chloride (PPN$^+$Cl$^-$), and the mixture was dissolved in dry dichloromethane. The solution was stirred for 10 min; a few drops of dry diethyl ether were added in order to aid the precipitation of LiCl. The mixture was filtered through a plug of Celite and the filtrate stripped of solvents. The resulting yellow orange crystalline solid was recrystallized from dry dichloromethane and tetrahydrofuran.

Bis(triphenylphosphoranylidene)ammonium (Benzoyl)tricarbonyl[2-(phenyl-$\kappa C^{2'}$),pyridine-κN]rhenate(I), PPN-2a. Elemental anal. Calcd for $C_{57}H_{43}N_2O_4P_2Re$: C, 64.16; H, 3.97; N, 2.63; Re, 17.45. Found: C, 64.26; H, 4.09; N, 2.68; Re, 13.35. IR (CH_2Cl_2): ν 1967 (s, Re−CO), 1859 (s, Re−CO), 1841 (s, Re−CO), 1541 (w, Ph−*CO*) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.82 (m, 3H), 6.95 (t, 1H, $J = 6.9$ Hz), 7.05 (t, 2H, $J = 6.0$ Hz), 7.38−7.48 (m, 26 H), 7.56−7.64 (m, 8H), 7.76 (d, 1H, $J = 7.8$ Hz), 8.16 (d, 1H, $J = 6.6$ Hz), 8.99 (d, 1H, $J = 5.4$ Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 118.3, 120.1, 120.5, 123.5, 125.8, 125.9, 126.5, 126.6, 126.8 (d, PPN$^+$, $J = 107$ Hz), 127.3, 129.4 (d, PPN$^+$, $J = 13$ Hz), 132.0 (d, PPN$^+$, $J = 13$ Hz), 133.8 (s, PPN$^+$), 135.2, 141.8, 146.8, 153.8, 157.2, 167.5, 200.9 (CO), 205.8 (CO), 208.3 (CO), 276.1 (Ph−*CO*−Re) ppm.

Bis(triphenylphosphoranylidene)ammonium (Acetyl)tricarbonyl-[2-(phenyl-$\kappa C^{2'}$),pyridine-κN]rhenate(I), PPN-2b. Elemental anal. Calcd for $C_{52}H_{41}N_2O_4P_2Re$: C, 62.08; H, 4.11; N, 2.78. Found: C, 60.95; H, 4.21; N, 2.50. IR (CH_2Cl_2): ν 1964 (s, Re−CO), 1853 (s, Re−CO), 1841 (s, Re−CO), 1561 (w, CH_3−*CO*) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 1.99 (s, 3H, CH_3CO), 6.90 (m, 4H), 7.66−7.36 (m, 31 H), 7.79 (d, 1H, $J = 8.3$ Hz), 8.09 (dd, 1H, $J = 7.3$ Hz, $J = 0.7$ Hz), 8.87 (d, 1H, $J = 4.8$) ppm. ^{13}C NMR (CD_2Cl_2): δ 53.0, 120.4, 122.3, 122.9, 128.3 (d, PPN$^+$, $J = 108$ Hz), 129.8, 129.9, 131.4 (m, PPN$^+$), 134.1 (m, PPN$^+$), 135.7 (PPN$^+$), 137.5, 143.1, 147.7, 155.5, 169.0, 202.9 (CO), 207.9 (CO), 210.4 (CO), 278.9 (CH_3−*CO*−Re) ppm.

Crystallographic Data Related to the Structure Determination of PPN-2b. Acquisition and processing parameters are displayed in Table 1. A total of 5095 reflections were collected, $2.5° < \theta < 26.3°$, on a Nonius CAD4-F diffractometer using Mo Kα graphite-monochromated radiation ($\lambda = 0.710\,73$ Å), with 4489 reflections having $I > 3\sigma(I)$. Empirical absorption corrections were obtained from the ψ scans of 7 reflections; absorption factors, 0.74/1.00. The structure was

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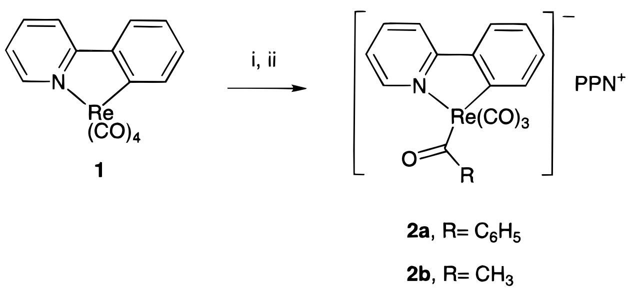
Table 1. Abbreviated Acquisition and Processing Data

formula	$C_{52}H_{41}N_2O_4P_2Re{\cdot}CH_2Cl_2$
mol wt	1091.00
cryst syst	monoclinic
space group	*C*1*c*1
a (Å)	20.747(1)
b (Å)	14.5150(9)
c (Å)	18.162(2)
β (deg)	121.196(6)
V (Å^3)	4678(1)
Z	4
ρ_{calc} (g cm^{-3})	1.55
μ (mm^{-1})	2.861
temp (K)	173
λ (Å)	0.710 73
R^a	0.029
$R_w{}^a$	0.041

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_c)^2]^{1/2}$. See ref 7b.

Scheme 1[a]



[a] (i) RLi (1 equiv), −30 °C, Et$_2$O. (ii) PPN$^+$Cl$^-$ (1 equiv), room temperature, CH$_2$Cl$_2$.

solved using direct methods and refined against |*F*|. Hydrogen atoms were introduced as fixed contributors. The absolute structure was determined by refining Flack's *x* parameter (575 parameters). For all computations the Nonius OpenMolEN package was used.[7a]

Discussion and Results

The reaction of a pale yellow solution of the pyridine rhenium chelate **1** with PhLi (or MeLi) at low temperature yielded an orange-yellow solution of the lithium salts of **2a** (or **2b**). The moderately air-sensitive lithium salts were converted by a metathesis reaction into the more stable PPN$^+$ salts, e.g., PPN-**2a** and PPN-**2b** (Scheme 1).

The two acyl−metalate complexes were air- and temperature-stable. Spectroscopic analyses of the two PPN$^+$ acyl−rhenates provided information consistent with the proposed structures and were in agreement with data reported for nonchelated analogues.[8] IR spectra of PPN-**2a** and PPN-**2b** in dichloromethane displayed three intense bands for the Re(CO)$_3$ moiety at 1967, 1859, and 1841 cm^{-1} and at 1964, 1853, and 1841 cm^{-1}, respectively. The characteristic carbonyl C−O stretching absorption bands of the benzoyl (PPN-**2a**) and acetyl (PPN-**2b**) groups were detected at 1541 and 1561 cm^{-1}, respectively. ^{13}C NMR spectra of PPN-**2a** and PPN-**2b** recorded at room temperature displayed at around 200 ppm a group of three resolved signals that were assigned to the three magnetically inequivalent facial carbonyl ligands of the Re(CO)$_3$ moiety. The ^{13}C resonances of the acyl carbonyl carbon atoms were detected at 276.1 and 278.9 ppm for PPN-**2a** and PPN-**2b**, respectively. Similar results for the ^{13}C resonance of the acyl carbon were reported recently by Casey and co-workers for Li$^+$[(η^5-C$_5$H$_5$)(CO)$_2$Re(C═O)(η^5-C$_5$H$_4$)Re(CO)$_3$]$^-$ and Li$^+$[(CO)$_2$Re(C═O)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^-$.[9,10] Recrystallization of PPN-**2b** from pure dichloromethane afforded yellow-orange monoclinic crystals suitable for X-ray diffraction analysis (Figure 1).

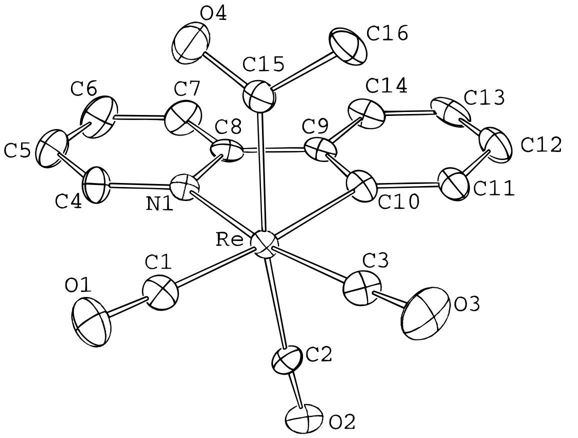


Figure 1. ORTEP drawing and atom-numbering scheme of the molecular structure of **2b**. Hydrogen atoms, the countercation PPN$^+$, and the molecule of CH$_2$Cl$_2$ present in the unit cell have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected interatomic bond distances (Å): Re−C1, 1.884(7); Re−C2, 2.014(7); Re−C3, 1.909(8); Re−N1, 2.168(7); Re−C10, 2.227(7); Re−C15, 2.149(7); C1−O1, 1.162(9); C2−O2, 1.158(9); C3−O3, 1.16(1); C15−O4, 1.232(9); C15−C16, 1.513(9). Selected bond angles (deg): C1−Re−C2, 96.7(3); C1−Re−C3, 90.9(4); C1−Re−N1, 97.9(3); C1−Re−C10, 173.2(3); C1−Re−C15, 95.6(3); C2−Re−C3, 87.5(3); C2−Re−N1, 94.0(3); C2−Re−C10, 84.4(3); C2−Re−C15, 167.5(3); C3−Re−N1, 170.8(4); C3−Re−C10, 95.8(3); C3−Re−C15, 94.5(3); N1−Re−C10, 75.3(3); N1−Re−C15, 82.1(3); C10−Re−C15, 83.0(2).

The molecular structure of PPN-**2b** determined at −100 °C fits the symmetry space group *C*1*c*1. Selected bond lengths and angles that are listed in the caption of Figure 1 illustrate a distorted octahedral configuration of the metal center. The nonlinearity of the C2−Re−C15 arrangement is consistent with similar observations reported for neutral chelated (tricarbonyl)(phosphine)manganese(I) complexes.[11]

The C2−Re−C15 angle of 167.5(3)° suggests that the acetyl moiety significantly bends toward the 2-phenylpyridine. The acetyl group is twisted with respect to the best plane containing atoms N1, Re, C15, and C3 as indicated by the dihedral angles O4−C15−Re−N1 (28°) and C16−C15−Re−C3 (23°). The phenyl and pyridyl groups of the 2-phenylpyridine ligand are coplanar and, with exception of slightly shortened N1−C4 and N1−C8 bond lengths, do not reveal important structural distortions. The acyl carbon to rhenium (C15−Re) bond distance of 2.149(7) Å is slightly longer than C═Re bonds reported for neutral or cationic carbonylrhenium alkylidene complexes[12] but nevertheless shorter than a typical single σ-type C−Re bond such as C10−Re (2.227(7) Å) or the bond between the rhenium center and the acetyl carbon atom in (C$_5$H$_5$)Re-

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$(CO)_2(CH_3)(C(O)CH_3)$.[13] This indicates that the acyl carbon to rhenium bond possesses a partial double bond character probably conferred by π-type orbital interactions between the metal fragment and the π-accepting acyl group. The long C2−Re bond distance (2.014(7) Å) as compared to C1−Re (1.884(7) Å) and C3−Re (1.909(8) Å) reflects the weakening of bonding interactions between the charged metal center and the carbonyl ligand C2−O2. It must be pointed out that such important differences in interatomic bond distances are not observed for the corresponding carbonyl carbon to oxygen bonds C1−O1, C2−O2, and C3−O3, which possess similar oxygen to carbon bond distances. The carbonyl carbon to oxygen bond distance C15−O4 of 1.232(9) Å is comparable to that observed in other acyl-metal complexes.[14]

The regioselective addition of an organolithium reagent to an axial carbonyl ligand in both examples presented here can be interpreted as the result of the electron-releasing properties of the bidentate phenylpyridine ligand deactivating the equatorial carbonyl ligands toward the addition of nucleophiles.[15] Thus, this effect favors a kinetically controlled nucleophilic addition to an axial carbonyl ligand. Moreover, for the anionic acyl−metal product, the presence of a carbonyl trans to the acyl group may stabilize the complex through redistribution of the electron density by a direct trans influence and through the π-acidic planar phenylpyridine bidentate ligand. On the basis of molecular orbital calculations carried out for $(CO)_5MnCOCH_3$, Casey and co-workers concluded that the selective addition of a nucleophile at a CO ligand was the result of an orbitally controlled reaction.[16] However, too many closely spaced empty levels associated with both the acyl and coordinated CO which take part in the lowest unoccupied molecular orbital precluded the prediction of the preferential site of nucleophilic attack.

In conclusion, the rationale drawn for both the reactivity of **1** and the structure of **2b** is consistent with our findings reported previously for the homologous manganese series.[5] The cis relationship between the acetyl group of PPN-**2b** and the phenyl fragment together with the slight bending of the acetyl group toward the chelating phenylpyridine ligand could favor, on the one hand, the reductive-elimination processes that we observed at room temperature with the more reactive anionic acyl−manganese complexes and, on the other hand, in the step leading to neutral chelated η^3-benzyl manganese complexes, the cis migration of the phenyl ring attached to the pyridine ligand onto the transient carbene moiety presumably formed by O-alkylation of the acyl group when methyl triflate is added to the medium.[5] It is noteworthy that the treatment of the rhenium anions **2a** and **2b** with methyl triflate yielded neither η^3-benzyl rhenium complexes nor alkoxycarbene complexes. Instead, according to GC−MS analysis, mixtures of various organic decomposition products and green rhenium-containing residues were obtained.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of PPN-**2b**·CH_2Cl_2 is available on the Internet only. Access information is given on any current masthead page.

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