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Platinum(II) and Platinum(IV) Acyl and Formyl Complexes

Stefan Reinartz, Maurice Brookhart,* and Joseph L. Templeton*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

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Summary: An unprecedented monomeric platinum(IV) formyl complex has been prepared by analogy to the synthetic route used to form platinum(IV) acyl complexes.

Transition-metal formyl complexes have been proposed as intermediates in Fischer−Tropsch syntheses, and their isolation, characterization, and reaction chemistry remain important research targets.[1−3] Stable formyl complexes have been described for several late transition metals, including iron, ruthenium, rhodium, and iridium,[4,5] but are unknown for platinum monomers. A formyl ligand bound to a platinum cluster has been recently characterized.[6]

The stability of organometallic d^6 octahedral platinum(IV) complexes TpPt(R)(R′)H (Tp = hydridotris(pyrazolyl)borate; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate; R, R′ = combinations of alkyl, hydride, and aryl groups)[7] reflects robust tridentate coordination of the tris(pyrazolyl)borate ligand,[8] which inhibits formation of the five-coordinate platinum(IV) precursor to reductive elimination.[9] We have recently reported a convenient synthesis of Tp′Pt(CH_3)(CO) (**1**) which is initiated via protonation of Tp′PtMe_2H before trapping with CO.[7g,10] The high CO stretching frequency of 2057

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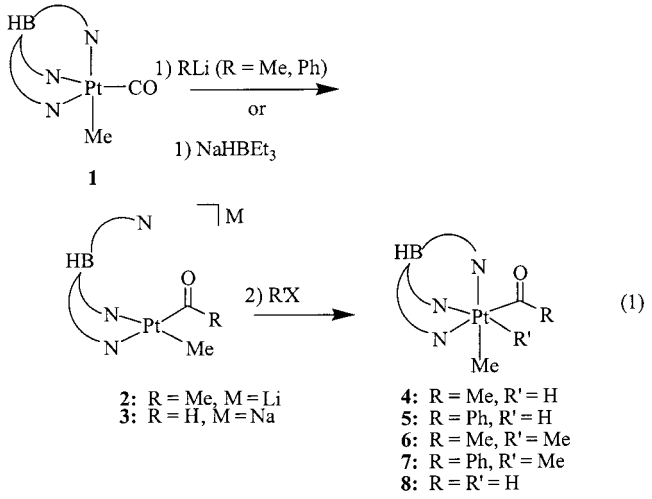
Table 1. Selected NMR Data for Anionic Platinum(II) Complexes 2 and 3

complex	δ(Pt−CH_3)/ ppm	δ(Pt−CH_3)/ ppm	$^1J_{Pt-C}$/ Hz	δ(Pt−C(O)R)/ ppm	$^1J_{Pt-C}$/ Hz
2 (acetyl)	0.33	−21.9	875	243.9	*a*
3 (formyl)	0.48	−16.0	920	237.0	1260

[a] Coupling to platinum was not resolved.

cm^{-1} (KBr) in **1** suggests that nucleophilic attack on the carbonyl ligand by anionic nucleophiles might be feasible. Subsequent addition of an electrophile to the resulting anionic platinum(II) species followed by coordination of the third Tp′ arm could allow access to new platinum(IV) compounds. We report here use of this strategy to form anionic platinum(II) formyl and acyl complexes, which, upon protonation or methylation, yield neutral platinum(IV) products.

Reaction of the methyl carbonyl complex **1** with MeLi in THF-d_8 forms the anionic platinum(II) acyl complex [Li][(η^2-Tp′)PtMe(C(=O)Me)] (**2**), as assessed by NMR spectroscopy (eq 1). At 193 K, both ^{1}H and ^{13}C NMR



(1)

spectra display unique resonances for each methine and methyl group of the Tp′ ligand, indicating a chiral metal center. A broad singlet at 2.04 ppm in the ^{1}H NMR spectrum is assigned to the acyl methyl group, and the platinum-bound methyl group is seen as a singlet at 0.33 ppm. The ^{13}C{^{1}H} NMR spectrum of **2** displays resonances at 243.9 ppm for the metal-bound acyl carbon and at 42.1 ppm ($^2J_{Pt-C}$ = 320 Hz) for the acyl methyl carbon. The carbon of the platinum-bound methyl group resonates upfield at −21.9 ppm ($^1J_{Pt-C}$ = 875 Hz) (Table 1). NMR data are compatible with a square-planar geometry for anion **2** with a bidentate Tp′ ligand, a methyl group, and an acetyl group in the platinum(II) coordination sphere. In the presence of excess methyllithium, the anionic acyl complex **2** rapidly decomposes below room temperature.

Having shown that the carbonyl ligand in Tp′PtMe(CO) (**1**) is susceptible to nucleophilic attack, this strategy was applied to the synthesis of platinum(IV) acyl complexes on a preparatory scale. Although platinum acyl complexes have been studied both as model systems for insertion chemistry[11−14] and as intermediates in processes such as hydroformylation and hydroacylation,[15,16] it was not until 1998 that stable platinum(IV) acyl hydride species were reported by Steinborn and co-workers.[17]

Table 2. Selected NMR Data for Neutral Platinum(IV) Complexes 4−8

complex	δ(Pt−CH_3)/ ppm	δ(Pt−H)/ppm	δ(Pt−CH_3)/ ppm	$^1J_{Pt-C}$/ Hz	δ(Pt−C(O)R)/ ppm	$^1J_{Pt-C}$/ Hz
4	1.30	−19.16	−20.7	639	197.4	859
5	1.05	−18.49	−17.8	628	197.9	*a*
6	1.40		−7.4	710	198.2	915
7	1.54		−4.2	700	193.0	1002
8	1.33	−19.18	−16.2	660	191.6	869

[a] Coupling to platinum was not resolved.

Protonation of the acyl anion **2** with HCl·Et_2O occurs at platinum to yield the chiral platinum(IV) complex Tp′PtMe(C(=O)Me)H (**4**) (eq 1). The solid-state IR spectrum of Tp′Pt(CH_3)(C(=O)CH_3)H (**4**) (KBr) shows an absorption at 2540 cm^{-1} for the B−H stretch of the Tp′ ligand, indicative of a κ^3 coordination mode.[18] A broad absorption at 2258 cm^{-1} for the Pt−H stretch and an intense absorption at 1668 cm^{-1} for the acyl stretch are also seen. The ^{1}H NMR spectrum of **4** indicates a chiral metal center. The acyl methyl group appears at 2.54 ppm ($^3J_{Pt-H}$ = 25 Hz). The platinum-bound methyl group at 1.30 ppm displays typical two-bond coupling to platinum of 70 Hz,[19] while the lone platinum-bound hydride resonates at −19.16 ppm ($^1J_{Pt-H}$ = 1427 Hz). Diagnostic signals are observed in the ^{13}C NMR spectrum at 197.4 ppm ($^1J_{Pt-C}$ = 859 Hz), 44.5 ppm ($^2J_{Pt-C}$ = 252 Hz), and −20.7 ppm ($^1J_{Pt-C}$ = 639 Hz), assigned to the carbonyl carbon atom, the acyl methyl group, and the carbon atom of the platinum-bound methyl group, respectively (Table 2). Similarly, reaction of the methyl carbonyl complex **1** with methyllithium followed by methylation, or with phenyllithium followed by protonation or methylation, leads to the synthesis of stable platinum(IV) acyl complexes (**5**−**7**) in good yields after chromatography and recrystallization (eq 1, Table 2). Spectral data for the chiral benzoyl hydride complex **5** are congruent with those of complex **4** (Table 2). Note the unique collection of cis ligands (methyl/phenyl, hydride, acyl) in complexes **4** and **5**.

Both acyl dimethyl complexes **6** and **7** display mirror symmetry according to ^{1}H and ^{13}C NMR spectra. The

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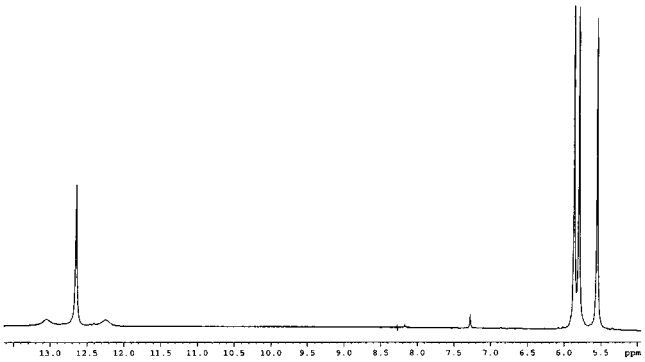

Figure 1. 400 MHz ^{1}H NMR spectrum of [Na][(κ^2-Tp′)-PtMe(C(═O)H)] (**3**), showing formyl and Tp′ C*H* resonances (243 K).

carbon resonance for the platinum-bound methyl groups in the benzoyl complexes moves downfield roughly 13 ppm relative to analogous resonances in acetyl complexes **4** and **5** (−7.4 ppm in the dimethyl acetyl complex **6** and −4.2 ppm in the dimethyl benzoyl complex **7**; Table 2). The ^{1}H NMR spectrum of the dimethyl acetyl complex **6** shows a broad resonance at 2.18 ppm ($^3J_{Pt-H}$ = 10 Hz) for the acetyl methyl protons, and the acetyl methyl carbon appears at 36.0 ppm ($^2J_{Pt-C}$ = 180 Hz) in the ^{13}C NMR spectrum.

Reaction of the methyl carbonyl reagent **1** with Na[Et_3BH] solution in THF-d_8 leads to the formation of the anionic platinum(II) formyl complex [Na][(η^2-Tp′)-PtMe(C(═O)H)] (**3**), as assessed by NMR spectroscopy (eq 1, Table 1). At 243 K, both ^{1}H and ^{13}C NMR spectra indicate chirality at metal. A singlet at 12.66 ppm in the ^{1}H NMR ($^2J_{Pt-H}$ = of 327 Hz) is assigned to a formyl proton (Figure 1). The platinum-bound methyl group is seen as a singlet at 0.48 ppm. The ^{13}C{^{1}H} NMR spectrum of **3** contains a resonance at 237.0 ppm that is positive in a DEPT 90 experiment and displays one-bond coupling to platinum of 1260 Hz. This resonance splits into a doublet ($^1J_{C-H}$ = 150 Hz) in the absence of proton decoupling, consistent with a metal-bound formyl moiety.[1]

At 193 K, two formyl species are present in solution, as indicated by resonances at 12.81 and 11.85 ppm in a 2:1 ratio, corresponding to a $\Delta G°$ value of about 0.3 kcal/mol. These two signals coalesce at 201 K, and a $\Delta G^‡$ value for conversion of the minor to the major isomer of ca. 8.8 kcal/mol has been calculated.[20] This exchange process is assigned to hindered formyl rotation about the Pt−C bond.[21]

Protonation of the anionic platinum(II) formyl complex **3** could conceivably form H_2 and regenerate **1**, or

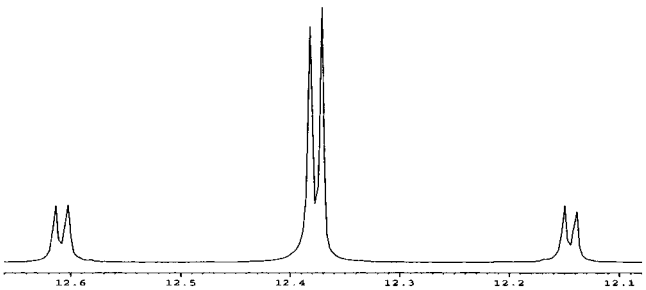

Figure 2. 400 MHz ^{1}H NMR of Tp′PtMe(C(═O)H)H (**8**), showing the formyl resonance.

protonation could occur on the pendant nitrogen atom or at the formyl oxygen or at the metal. In fact, protonation of **3** at 193 K occurs at the metal to form chiral Tp′PtMe[(C(═O)H)]H (**8**), presumably because of the formation of a preferred octahedral coordination geometry.[22] The formyl resonance at 12.38 ppm in the room-temperature ^{1}H NMR spectrum appears as a doublet ($^3J_{H-H}$ = 4.4 Hz) with platinum satellites ($^2J_{Pt-H}$ = 186 Hz) (Figure 2). A hydride resonance at −19.18 ppm appears as a doublet due to coupling to the formyl proton ($^3J_{H-H}$ = 4.4 Hz, $^1J_{Pt-H}$ = 1418 Hz). The protons of the platinum-bound methyl group resonate at 1.33 ppm ($^2J_{Pt-H}$ = 71 Hz), typical of a platinum(IV) methyl complex.[7a,c,19] The ^{13}C{^{1}H} NMR spectrum of **8** contains a resonance at 191.6 ppm assigned to the formyl carbon that is positive in a DEPT 90 experiment and splits into a doublet in the proton-coupled ^{13}C NMR spectrum ($^1J_{C-H}$ = 161 Hz). Attempts to isolate the platinum(IV) formyl hydride complex **8** were unsuccessful; the complex readily decarbonylates to Tp′PtMe$(H)_2$.

In summary, we have successfully prepared a number of unique platinum(IV) acyl complexes from Tp′PtMe(CO). The same methodology, nucleophilic attack on coordinated CO, has been employed with Na[Et_3BH] as the nucleophilic reagent to prepare elusive platinum formyl complexes. The array of methyl, formyl, and hydride ligands in a cis arrangement in Tp′PtMe[(C(═O)H)]H is particularly noteworthy.

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Supporting Information Available: Text giving synthetic details and characterization data for the compounds prepared in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) For analysis of coalescence in a 2:1 population system, see: Baker, M. V.; Brown, D. H.; Somers, N.; White, A. H. *Organometallics* **2001**, *20*, 2161 and ref 17 therein.

(21) Hindered formyl rotation in **3** may be due to ion pairing.[4c]

(22) For a paper dealing with varying protonation sites in platinum(II) complexes, see: Hinman, J. G.; Baar, C. R.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 563.