electron-deficient complexes, where the thermodynamic driving force for the observed disproportionation to give \( \text{Cp*Hf}[\text{P(CMe}_3]_2\text{Cl}_2 \) an intermediate \( \text{Cp*Hf}(\text{H})\text{Cl}_2 \) species located by X-ray diffraction. A number of late-transition-metal dimer. In the heterobimetallic complex \( \text{Cp*Hf}[\text{P(CMe}_3]_2\text{Cl}_2 \), the metal centers are probably electronically strongly stabilized. This makes it likely that intermediate stabilization of complexes with complicated stoichiometries. Bercaw et has enabled us to obtain soluble, crystalline \( \text{CP*Zr} \) hydride complexes. For these sterically and electronically strongly \( \text{Fe}_2(\text{b-alkoxides}) \) promotes comproportionation rather than disproportionation. Presently we are investigating a range of \( \text{CP*M} \) hydrides (\( \text{M} = \text{Zr}, \text{Hf} \)) with varying stoichiometries and their interaction with Lewis bases to get a more complete view of the structure-determining factors in strongly electron-deficient early-transition-metal hydrides.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supplementary Material Available: Experimental details, spectral and analytical data for all compounds, data of structure determination, crystal data, and lists of positional and thermal parameters for 4 (15 pages); a listing of observed and calculated structure factors for 4 (26 pages). Ordering information is given on any current masthead page.

First Prototype of Neutral Diacyl Complexes of Platinum(II) and Related Acyl(alkyl) Complexes of Platinum(II)

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Summary: The acyl(carbonyl) complex \( \text{cis-[Pt(COPh)(CO)(PPh}_3]_2 \) reacts with \( \text{PhLi} \) to yield the neutral dibenzoyl complex \( \text{cis-[Pt(COPh)(PPh}_3]_2 \) in 34
c% yield. The crystallographic data of 3a indicate that it is disposed in a distorted square-planar geometry with two benzoyl carboxyls in the \( \delta \)-trans configuration. The analogous reaction of the cationic 2a with \( \text{MeLi} \), however, gives three products: \( \text{cis-[Pt(COPh)(COMe)(PPh}_3]_2 \) (3b), \( \text{cis-[Pt(COPh)(Me)(PPh}_3]_2 \) (4), and \( \text{Pt(COPh)(Me)(CO)}\text{PPh}_3 \) (5a) in a relative ratio of 1:2.5:3 in 55
c% yield. In a similar reaction carried out in the presence of extra \( \text{PPh}_3 \), only 3b and 4 were obtained, in a 1:3.5 ratio in 90
c% total yield. The structures of the complexes 4 and 5a were determined by X-ray crystallography, and both are square planar. In 5a, the \( \text{PPh}_3 \) was found trans to the benzoyl ligand. The replacement of a \( \text{PPh}_3 \) in 5a by \( \text{CO} \) gives 5a and its regio isomer 5b, whose \( \text{PPh}_3 \) is in trans to the methyl group. The complex 5b is kinetically favored but thermodynamically unstable. These substitution reactions are reversible with the equilibria in favor of 4.

The rare diacyl complexes of the prototype RC(OMC)(OR)' (wherein R and R' are hydrocarbyls) are either anionic or stabilized by bridging structures.

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The rare diacyl complexes of the prototype RC(OMC)(OR)' (wherein R and R' are hydrocarbyls) are either anionic, stabilized by bridging structures.
ously, all of them are found in d6 octahedral systems. In d8 square-planar systems, such diacyl species were proposed as key intermediates in carbonylative coupling reactions. However, such complexes have not yet been isolated. Reported herein are the first examples of neutral diacyl complexes of Pt(II), as well as the unprecedented acyl(alkyl) and acyl(alkyl)(carbonyl) complexes of Pt(II).

Treatment of trans-Pt(COCOPh)(Cl)(PPh3)2 (1) with AgBF4 in dichloromethane at -29 °C led to cis-[Pt(OCOPh)(CO)(PPh3)][BF4] (2a). After the removal of precipitated AgCl, the temperature was lowered to -63 °C. The addition of 1.1 equiv of PhLi to the reaction solution resulted in instantaneous formation of the cis dibenzoyl complex, cis-Pt(CO)(PPh3)(PPh3) (3a). Recrystallization of 3a from CH2Cl2/Me2O afforded golden yellow, crystalline material in 54% isolated yield.

The dibenzoyl compound 3a has been spectroscopically and crystallographically characterized. Its ORTEP plot in Scheme I shows that 3a is in a distorted square-planar geometry with the benzoyl ligands in the cis position. The bond angles θ(Pt-1)-Pt-Pt-2, 80.5° (9) and θ(Pt-1)-Pt-C-1, 141.4° (10), reveal the bond angles θ(Pt-1)-Pt-2, 289.6° (3a) (9) and θ(Pt-1)-Pt-C-1, 50°. Total reflections, 7986; observed reflections, 5276 I > 2σ(I).

Selected spectroscopic data of 3a: IR (KBr) νCO = 1613, 1596 cm⁻¹; 13C NMR (CDCl3) δ 145.0 (a-1), 136.0 (b-1), 134.0 (c-1), 131.5 (d-1), 129.0 (e-1), 127.5 (f-1), 126.5 (g-1), 125.0 (h-1), 115.0 (i-1), 114.5 (j-1), 103.0 (k-1), 90.0 (l-1), 85.0 (m-1), 80.0 (n-1), 75.0 (o-1), 70.0 (p-1), 65.0 (q-1), 60.0 (r-1), 55.0 (s-1), 50.0 (t-1), 45.0 (u-1), 40.0 (v-1), 35.0 (w-1), 30.0 (x-1), 25.0 (y-1), 20.0 (z-1).
M–C(sp²) and M–C(sp) bonds. The rather short Pt–CO bond indicates that the methyl group may facilitate the backbonding, which presumably is responsible for the unusual stability of this carbonyl ligand in 5a. The separation of 3b and 4 from their mixtures was not successful. The addition of PPh₃ to the solution of 5a caused complete conversion of 5a to 5b.¹² Complex 4 is the first structurally characterized acyl(alkyl) compound of Pt(II).¹³,¹⁴ The Pt–P bond of the phospine trans to the methyl group is 0.04 Å shorter than the Pt–P bond trans to the benzyl group. The acetyl(benzoyl) complex 3b was mainly identified by spectroscopic methods.¹⁵ Two acyl vibrations at 1628 and 1605 cm⁻¹ in the IR and a ³¹P NMR resonance of doublets of doublets with ⁴J(P–P) = 1568.1 Hz strongly support the cis diacyl structure.

At ambient temperature, the complex 4 in CDC₁₅ slowly decomposed to give acetophenone as the predominant product.¹⁶ Along with several unidentified complexes. The formation of acetophenone was substantially accelerated, when 1 atm of CO was applied to the solution of 4. Reaction of 4 with CO also led to the formation of an intermediate 5b in <40% conversion. Complex 5b eventually disappeared, while 5a was formed in 30% yield. The bubbling of CO into the solution of 5a did not give any 5b.

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Supplementary Material Available: An experimental section, tables of complete crystal data, complete lists of bond lengths and angles, atomic coordinates, and thermal parameters, and ORTEP drawings for 3a, 4, and 5a (21 pages); listings of structure factors for 3a, 4, and 5a (54 pages). Ordering information is given on any current masthead page.

Complex 5b exhibited NMR patterns¹⁷ analogous to those of 5a, except for the relatively large coupling constant, ⁴J(P–P) = 1967 Hz, in the ³¹P spectrum. Accordingly, we assign 5b as an isomer of 5a, in which the PPh₃ is trans to the methyl group rather than cis. The equilibria between 5a and 4, as well as between 5b and 4, could simply result from the substitution of either PPh₃ in 4 by CO. This is reasonable, since the Pt–P bond of the PPh₃ trans to the benzoyl group is weaker. Therefore, 5b is kinetically favored.

The overall reaction mechanism has not been fully elucidated. However, the NMR study of the reaction between 2a and MeLi at -40 °C showed that 3b was not the primary product. The decomposition of 3b yielded neither 4 nor 5a. An intermediate 6, which presumably is formed by nucleophilic attack of MeLi at the metal center of 2a, is proposed. Through 6, 3b could be independently formed by CO insertion. Meanwhile, 4 and 5a could be produced by the loss of the coordinated CO and PPh₃, respectively, from 6.

(12) Selected spectroscopic data of 4: IR (KBr) ν CO = 1604 cm⁻¹; ³¹P NMR δ 24.38 (J P–Pt = 14.3, J Pt–P = 2196.3 Hz), 20.04 (J P–Pt = 1423.2 Hz); ¹H NMR δ 0.33 (CH₃, ddt, J H–P = 9.2, J Pt–P = 6.2 Hz, J Pt–Pt = 68.4 Hz).
(13) 4 C₆H₅OP₂Pt, n, a = 11.290 (2), b = 17.837 (4), c = 18.306 (4) Å, β = 98.74 (2)°, V = 3847.6 A³, Z = 4, μ = 4.01 mm⁻¹; total reflections, 4746; observed reflections, 3032 I > 1.5σ(I) R = 0.048, R = 0.033. Pt-P(1), 2.297 (3); Pt-P(2), 2.338 (3); Pt-C, 2.18 (1); Pt-C(1), 2.03 (1); C(1)–O(1), 1.17 (2).
(15) Selected spectroscopic data of 3b: IR (KBr) ν CO = 1628, 1605 cm⁻¹; ³¹P NMR δ 15.49 (J P–Pt = 18.5, J Pt–Pt = 1568.1 Hz), 13.91 (J P–Pt = 1675.9 Hz); ¹H NMR δ 1.50 (CH₃, dt, J H–Pt = 0.65 Hz, J Pt–Pt = 15.3 Hz).
(16) ¹H NMR δ 2.60 (CH₃); GC-MS, M⁺ = 210.
(17) Selected spectroscopic data of 5b: ³¹P NMR δ 21.5 (J P–Pt = 1967 Hz); ¹H NMR δ 0.67 (CH₃, dt, J H–Pt = 6.2 Hz, J Pt–Pt = 72 Hz).