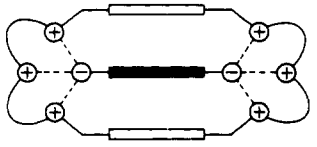
both for the most strongly bound dicarboxylates and for the $(CH_2)_n$ bridges separating the triammonium binding units in **1**-$6H^+$ (n = 7) and in **2**-$6H^+$ (n = 10). The smaller receptor **3**-$6H^+$ (n = 3) binds most strongly the shorter dicarboxylates.[1]

(4) The observation of a selectivity peak as a function of chain length reveals a *dominant structural factor* in dicarboxylate binding. Electrostatic interactions, which favor binding of anions of high charge density, were usually found to dominate both the strength and the selectivity of complexation;[1,2] the effect of ring size was already apparent for ligands of type **3**.[1]

(5) These complexation features may be extended to the selective binding of *biological anionic substrates*, in particular of dicarboxylate species. Thus, **1**-$6H^+$ binds preferentially the dianions *N*-acetyl-(L)-aspartate and *N*-acetyl-(L)-glutamate with respect to the dipeptide *N*-acetyl-(L)-glutamylglycinate, whereas the reverse holds for **2**-$6H^+$, in line with the chain lengths of these substrates.

(6) The high stabilities observed for the optimal coreceptor dicarboxylate substrate pairs results from the incorporation of two binding subunits in the macrocycle and from double (ditopic) carboxylate group–triammonium site binding; this is indicated by the low stabilities found for the single site interactions of butyrate with **2**-$6H^+$ (Table I) and of pimelate^{2-} or butyrate with the subunit reference ligand $^+H_3N(CH_2)_3NH^+_2(CH_2)_3NH_3^+$ (log $K_s \lesssim 2.0$).

(7) The *chain length selection* observed describes a *linear molecular recognition* process analogous to that found for dicationic substrates.[3-5] It may be attributed to *structural* complementarity between the dianionic substrate and the *ditopic coreceptor molecules* **1**-$6H^+$ and **2**-$6H^+$ in which the two binding subunits cooperate for substrate binding. The terminal anionic groups of the dicarboxylate would each interact with a triammonium unit of the coreceptor, the polymethylene chain stretching between the polymethylene bridges of the macrocycle. Highest stability of the complex corresponds to the best fit between substrate length and site separation of the receptor, as schematically represented by **18** and supported by consideration of



18

molecular models. Substrates that are either too short or too long form less stable complexes.

In conclusion, the present results demonstrate that it is possible to design coreceptor molecules for the selective multifunctional binding of molecular polyanions, in a way similar to the selective binding of diammonium cations of different chain lengths by macrotricyclic receptor molecules.[3,4] Ligand modification should allow to monitor the *molecular recognition* features, to devise *cocarriers* or *cocatalyst* for the selective transport or the catalytic modification of the bound substrate.[10] Such extensions of the present work are being pursued.

Registry No. 1, 81505-93-3; **1**·6HCl, 81505-94-4; **2**, 81505-95-5; **2**·6HCl, 81505-96-6; **3**·6HCl, 81505-97-7; **4**, 81505-98-8; **5**, 81505-99-9; **6**, 81522-66-9; **7**, 81506-00-5; **8**, 81506-01-6; **9**, 81506-02-7; **10**, 79130-37-3; **11**, 81506-03-8; **12**, 81522-67-0; **13**, 81506-04-9; **14**, 81506-05-0; **15**, 81506-06-1; **16**, 81506-07-2; **17**, 81506-08-3; oxalate^{2-}, 338-70-5; malonate^{2-}, 156-80-9; succinate^{2-}, 56-14-4; glutarate^{2-}, 56-16-6; adipate^{2-}, 764-65-8; pimelate^{2-}, 764-54-5; suberate^{2-}, 764-55-6; azelate^{2-}, 13479-16-8; sebacate^{2-}, 45130-36-7; maleate^{2-}, 142-44-9; fumarate^{2-}, 142-42-7; butyrate, 461-55-2; *N*-acetyl-L-aspartate^{2-}, 3130-81-2; *N*-acetyl-L-glutamate^{2-}, 3130-80-1; *N*-acetyl-L-glutamylglycinate^{2-}, 81506-09-4; 1,7-diaminoheptane, 646-19-5; 1,10-diaminodecane, 646-25-3.

(10) For a recent case of selective functionalization via association of acyclic dications and dianions see: Breslow, R.; Rajagopalan, R.; Schwarz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2905-2907.

Remarkable Dependency of Regioselectivity on the Catalyst Metal Species in the Hydroformylation of Trifluoropropene and Pentafluorostyrene

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It is well known that the hydroformylation of alkenes is an important reaction for the production of aldehydes.[1] Although precise studies on the mechanism of the reaction as well as applications of the reaction to organic synthesis have been extensively studied, little is known about the reaction of olefins bearing perfluoroalkyl or perfluoroaryl substituents.[2] Recently, it has been shown that the introduction of a trifluoromethyl or pentafluorophenyl group into a biologically active compound often brings about unique physiological activities.[3] For the synthesis of such compounds, 3,3,3-trifluoropropene (TFP) and pentafluorostyrene (PFS) are important fundamental building blocks. Accordingly, we have been studying the hydroformylation of TFP and PFS as one of the possible functionalizations of these building blocks using a variety of transition-metal catalysts and have found unique features of the reaction compared with the hydroformylation of ordinary alkenes. We will describe here unusually high regioselectivities and remarkable dependency of regioselectivity on the structure of catalyst species in the hydroformylation of TFP and PFS.

Hydroformylation of TFP was carried out with $Co_2(CO)_8$, $Ru_3(CO)_{12}$, $Rh_6(CO)_{16}$, and $PtCl_2(DIOP)/SnCl_2$,[4] which are typical hydroformylation catalysts. Results are listed in Table I.

As Table I shows, the reaction of TFP catalyzed by $Co_2(CO)_8$ gave (trifluoromethyl)propanals (TFMPA) in 95% yield where a highly regioselective (93%) formation of "normal" aldehyde, $CF_3CH_2CH_2CHO$ (3-TFMPA) was observed. In sharp contrast with $Co_2(CO)_8$, the rhodium carbonyl cluster $Rh_6(CO)_{16}$ exhibited extremely high catalytic activity and regioselectivity (96%) to give "isoaldehyde", $CF_3(CH_3)CHCHO$ (2-TFMPA). The platinum catalyst $PtCl_2(DIOP)/SnCl_2$ favored the formation of *n*-aldehyde, while $Ru_3(CO)_{12}$ gave isoaldehyde as main product, and in both cases, the formation of considerable amounts of hydrogenated product, $CF_3CH_2CH_3$, was observed. Addition of triphenylphosphine to the cobalt, ruthenium, and rhodium catalyst considerably decreased the catalytic activities but somewhat increases the ratio of isoaldehyde. Because $Rh_6(CO)_{16}$ gave excellent regioselectivity in the formation of 2-TFMPA, several other rhodium catalysts were employed to examine their catalytic activities as well as regioselectivities. Results are also summarized in Table I. The results clearly indicate that the rhodium(I) complexes bearing chlorine as ligand such as $RhCl(PPh_3)_3$ are less active than $HRh(CO)(PPh_3)_3$, Rh–C, and $Rh_6(CO)_{16}$, but the regioselectivity is almost the same in every case examined.

Consequently, it is disclosed that the nature of the central metal of the catalyst plays a key role in determining the regioselectivity of the reaction. Moreover, it should be noted that the metal species

(1) (a) Pino, P.; Piacenti, F.; Bianchi, M. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, pp 43-231. (b) Cornils, B. In "New Syntheses with Carbon Monoxide"; Falbe, J., Ed.; Springer-Verlag: Berlin, 1980; pp 1-225.

(2) Hydroformylation of hexafluoropropene was reported to give a mixture of hexafluoropropane (50%), alcohols (40%), and aldehydes (5-8%). See: Rudkovskii, D. M.; Imyanitov, N. S.; Gankin, V. Yu. *Tr. Vses, Nauchn Issled. Inst. Neftekhim. Protsessov.* **1960**, *121*; *Chem. Abstr.* **1962**, *57*, 10989. A patent claimed the reaction of heptadecafluorodecene, $CF_3(CF_2)_7CH{=}CH_2$, catalyzed by $Co_2(CO)_8$, which gave the corresponding alcohols or aldehydes. See: Roehrscheid, F. (Hoechst A. G.), Ger. Offen. 1973, 2163752; *Chem. Abstr.* **1973**, *79*, 78110m.

(3) For example: (a) Smith, F. A. *Chemtech* **1973**, 422. Filler, R. *Ibid.* **1974**, 722. (b) Lin, T.-S.; Chai, C.; Prusoff, W. H. *J. Med. Chem.* **1976**, *19*, 915.

(4) $PtCl_2(DIOP)/SnCl_2$ was prepared in situ by mixing $PtCl_2(PhCN)_2$, (-)DIOP, and $SnCl_2$ in toluene.

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Table I. Hydroformylation of 3,3,3-Trifluoropropene (TFP)[a]

catalyst	TFP[b] cat.	p,[c] atm (CO/H_2 = 1)	temp, °C	time, h	aldehydes[d] %	aldehydes[d] iso/n	alkane,[d] %
$Co_2(CO)_8$	50	130	100	20	95	7/93	0
$Co_2(CO)_8/PPh_3$	50	130	100	41	3	9/91	1
$PtCl_2(DIOP)/SnCl_2$	100	130	100	4	75	29/71	25
$Ru_3(CO)_{12}$	33	130	100	16	62	85/15	38
$Ru_3(CO)_{12}/PPh_3$	33	130	100	39	25	92/8	1
$Rh_6(CO)_{16}$	1200	110	80	5	98	96/4	2
$Rh_6(CO)_{16}/PPh_3$	1200	110	80	22	93	97/3	7
$Rh-C/P(OPh)_3$	1200	110	80	5	98	96/4	2
Rh–C	1200	110	80	5	96	96/4	4
$HRh(CO)(PPh_3)_3$	1200	110	80	5	95	95/5	5
$Rh-C/PPh_3$	1200	110	80	15	90	95/5	10
RhCl(dppb)	1200	110	80	22	42	97/3	<4
$RhCl(PPh_3)_3$	1200	110	80	22	30	96/4	<3
$RhCl(CO)(PPh_3)_2$	1200	110	80	22	23	95/5	<2
$RhCl_3 \cdot 3H_2O/PPh_3$	1200	110	80	22	17	96/4	<2

[a] All experiments were run with 130 mmol of TFP and 20 mL of toluene in a 200-mL stainless steel autoclave. [b] (mol TFP)/(g-atom of metal). [c] Initial pressure at room temperature. [d] Determined by GLC.

Table II. Hydroformylation of Pentafluorostyrene (PFS)[a]

catalyst	PFS[b] cat.	p,[c] atm (CO/H_2 = 1)	temp, °C	time, h	conv,[d] %	aldehydes[d] %	aldehydes[d] iso/n	alkane,[d] %
$Co_2(CO)_8$	21	80	90	12	67	54	21/79	9
$PtCl_2(DIOP)/SnCl_2$	100	80	90	4	100	76	49/51	20
$Ru_3(CO)_{12}$	33	80	90	17	49	22	74/26	25
$Rh_6(CO)_{16}$	5000	80	90	3	100	100	97/3	0
$RhCl(PPh_3)_3$	333	90	90	20	100	100	97/3	0
$HRh(CO)(PPh_3)_3$	5000	80	90	8	100	100	98/2	0

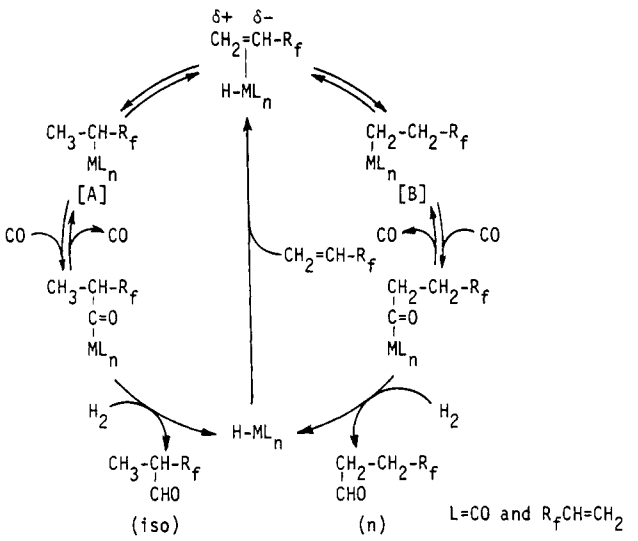
[a] All experiments were run with 100 mmol of PFS and 30 mL of benzene in a 200-mL stainless steel autoclave. [b] (mol PFS)/(g-atom of metal). [c] Initial pressure at room temperature. [d] Determined by GLC.

dependency of regioselectivity in the present reaction is extremely remarkable compared with that for propene, i.e., the reported regioselectivities in the formation of butanal using cobalt, platinum, ruthenium and rhodium catalysts are as follows:[1a] $Co_2(CO)_8$[5] [150 atm (CO/H_2 = 1/1), 110 °C] 94%, iso/*n* = 20/80; $PtCl_2(PPh_3)_2/SnCl_2$[6] [89 atm (CO/H_2 = 1/1), 66 °C] 90%, iso/*n* = 13/87; $Ru_3(CO)_{12}$[5] [150 atm (CO/H_2 = 1/1), 110 °C] 40%, iso/*n* = 26/74; $Rh_6(CO)_{16}$[7] [120 atm (CO/H_2 = 1/1), 70 °C] 51%, iso/*n* = 49/51.

Similar results were obtained in the hydroformylation of PFS, which are shown in Table II.

As Table II shows, rhodium catalysts exhibited high catalytic activity to give isoaldehyde, $C_6F_5(CH_3)CHCHO$, with excellent regioselectivity (97–98%) and quantitative yield, while $Co_2(CO)_8$ gave *n*-aldehyde as the major product, where the regioselectivity was not so high as that observed in the reaction of TFP. The ruthenium catalyst, $Ru_3(CO)_{12}$, showed a rather low catalytic activity, giving isoaldehyde as the major isomer, and a large amount of hydrogenated product, $C_6F_5CH_2CH_3$, was formed. The platinum catalyst, $PtCl_2(DIOP)/SnCl_2$, showed a high catalytic activity, but virtually no regioselectivity was observed and the hydrogenation of PFS took place as severe side reaction. As a whole, the metal species dependency of regioselectivity is very similar to that for TFP and it is also quite remarkable compared with that for styrene.[8]

Scheme I. Possible Mechanism for the Hydroformylation of TFP and PFS



Judging from the fact that the addition or introduction of tertiary phosphines to the catalyst brings about only a slight change of regioselectivity, in sharp contrast with the hydroformylation of propene or styrene using the same catalysts, either TFP or PFS must have a large binding constant with catalyst metal species, and thus they must act as important ligand that stabilizes the catalysts during the reaction.

The observed remarkable dependency of regioselectivity on the catalyst metal species may well be accommodated by taking into account the relative stability of alkylmetal species, i.e., R_f-

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(6) Shwager, I.; Knifton, J. F. (Texaco Development Co.), Ger. Offen. 1973, 2322751; *Chem. Abstr.* **1974**, *80*, 70327m.
(7) Booth, B. L.; Else, M. J.; Fields, R.; Haszeldine, R. N. *J. Organomet. Chem.* **1971**, *27*, 119.
(8) The reported regioselectivities in the formation of phenylpropanal are as follows: $Co_2(CO)_8$[9] [80 atm (CO/H_2 = 1/1), 120 °C] 46%, iso/*n* = 59/41; $PtCl_2(DIOP)/SnCl_2$[10] [250 atm (CO/H_2 = 1/1), 100 °C] 60%, iso/*n* = 57/43; $Rh_2Cl_2(CO)_4$[10] [62 atm (CO/H_2 = 1/1), 130 °C] 93%, iso/*n* = 43/57; $Rh_2Cl_2(CO)_4/PPh_3$[11] [62 atm (CO/H_2 = 1/1), 130 °C] 98%, iso/*n* = 72/28.
(9) Botteghi, C.; Consiglio, G.; Pino, P. *Chimia* **1972**, *26*, 141.
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(11) Ogata, I.; Ikeda, Y.; Asakawa, T. *Kogyo Kagaku Zasshi* **1971**, *74*, 1839.
(12) Imjanitov, N. S.; Rudkovskij, D. M. *J. Prakt. Chem.* **1969**, *311*, 712.

(Me)CH–MLn and $R_fCH_2CH_2$–MLn (L = CO and $R_fCH{=}CH_2$). A possible mechanism that can accommodate the unique results is depicted in Scheme I.

As trifluoromethyl and pentafluorophenyl groups (abbreviated as R_f) are strongly electron-withdrawing substituents, a negative charge on the α-carbon stabilizes α-(R_f)ethylmetal species, intermediate [A], while a positive charge on the α-carbon destabilizes intermediate [A]. Thus, if the MLn moiety induces a negative charge on the α-carbon, the branched intermediate [A] should be stabilized, and then the formation of isoaldehyde should be predominant: as a matter of course, if the MLn moiety induces a positive charge on the α-carbon, the unbranched intermediate [B] should be preferable, which leads to the formation of *n*-aldehyde. It is strongly suggested that the relative stability of the branched alkylmetal intermediate [A] increases in order R_f(Me)CH–CoLn < R_f(Me)CH–PtLn < R_f(Me)CH–RuLn < R_f(Me)CH–RhLn, i.e., the cobalt species may cause a fairly large positive charge on the α-carbon whereas the rhodium species may generate relatively large negative charge on the α-carbon, and the platinum and ruthenium species can be placed between cobalt and rhodium, in the present systems. However, a detailed understanding of the mechanisms of the present reactions should await further investigation.

Registry No. TFP, 677-21-4; PFS, 653-34-9; $Co_2(CO)_8$, 10210-68-1; $PtCl_2$(DIOP), 65582-87-8; $Ru_3(CO)_{12}$, 15243-33-1; $Rh_6(CO)_{16}$, 28407-51-4; Rh, 7440-16-6; $HRh(CO)(PPh_3)_3$, 17185-29-4; RhCl(dppb), 81725-30-6; $RhCl(PPh_3)_3$, 14694-95-2; $RhCl(CO)(PPh_3)_2$, 13938-94-8; $RhCl_3{\cdot}3H_2O$, 13876-89-6.

Solvent-Dependent Reactions of Carbon Dioxide with a Platinum(II) Dihydride. Reversible Formation of a Platinum(II) Formatohydride and a Cationic Platinum(II) Dimer, $[Pt_2H_3(PEt_3)_4][HCO_2]$

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Reactions of carbon dioxide with transition-metal compounds are relevant to CO_2 activation and catalysis of the water–gas shift reaction.[1] The properties of formate ion as a ligand have also attracted attention,[1-4] and metal-catalyzed decomposition of formate ion to yield CO_2 and metal hydride (reaction 1) has been

$$M^+ + HCO_2^- \rightleftharpoons M\text{–}O_2CH \rightleftharpoons M\text{–}H + CO_2 \qquad (1)$$

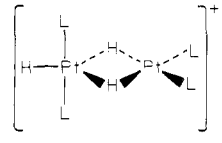
suggested as a key step in several systems that homogeneously catalyze the water–gas shift reaction.[3,5] We describe herein the unusual solvent dependence of the reactions of carbon dioxide with a sterically unhindered platinum(II) dihydride, a system that catalyzes the transformation of formic acid to carbon dioxide and hydrogen, and a mechanism for catalysis.

A toluene solution of predominantly *trans*-dihydrobis(triethylphosphine)platinum(II)[6] (**1**) under one atmosphere of carbon dioxide consists of an equilibrium mixture of **1** and *trans*-(formato)hydrobis(triethylphosphine)platinum(II) (**2**) (reaction 2).

$$\underset{\mathbf{1}}{PtH_2L_2} + CO_2 \overset{K}{\rightleftharpoons} \underset{\mathbf{2}}{\textit{trans}\text{-}PtH(O_2CH)L_2} \qquad (2)$$

A signal for **2** appears in the $^{31}P\{^1H\}$ NMR spectrum at δ 23.8 (s, $^1J_{Pt-P}$ = 2843 Hz). Examination of the ^1H NMR spectrum of this solution reveals a signal for formate hydrogen [H_a: δ 9.36 (d, br, $^4J_{H_a-H_b}$ = 4 Hz, $^3J_{Pt-H_a}$ = 47 Hz)] and a signal for hydride [H_b: δ −21.26 (td, $^2J_{P-H_b}$ = 16 Hz, $^4J_{H_b-H_a}$ = 4 Hz, $^1J_{Pt-H_b}$ = 1176 Hz)]. The presence of ^{195}Pt satellites for the formate hydrogen signal establishes that formate ion binds to platinum.[7] From the integrated intensities of the $^{31}P\{^1H\}$ NMR spectra, the equilibrium constant is approximately 2 atm^{-1} at 25 °C.

In polar solvents such as acetone or acetonitrile, **1** reacts rapidly with 1 atm of CO_2 at 25 °C to form a cationic platinum dimer, $[Pt_2H_3L_4]^+$ (**3**, L = PEt_3), and free formate ion. Addition of $LiBF_4$ yields a precipitate of $LiHCO_2$. Metathesis of **3a** with $NaBPh_4$ produces $[Pt_2H_3L_4][BPh_4]$ (**3b**), isolable as a yellow, crystalline, air-stable solid.[8] Analysis of the ^1H, ^{31}P, and ^{195}Pt NMR spectra of solutions of **3a** and **3b** reveals that the cation contains two inequivalent platinum centers, each bound to a pair of mutually equivalent triethylphosphine ligands. The metal centers are bridged by a pair of equivalent hydride ligands, and a third hydride ligand binds to one platinum, which is 5-coordinate.[9] These facts are consistent with the structure (**3**), and an analogous structure has been proposed for the cation $[Pt_2H_3(PPh_3)_4]^+$.[10]



3a = $[Pt_2H_3L_4][HCO_2]$
3b = $[Pt_2H_3L_4][BPh_4]$
L = PEt_3

Solvent strongly influences the reactions of carbon dioxide with **1**. Formation of **3a** in polar solvents may occur because these media stabilize charge-separated species; this solvent influence is primarily of *thermodynamic* origin. Support for this view comes from the observation that **3a** reverts to neutral monomers when extracted into toluene. Coordinating solvents could also exert a *kinetic* effect by displacing formate ion[11] from **2** to yield the solvated (S = solvent) cation $PtH(S)L_2^+$ (**4**), which could then react with **1** to form **3**.

That **3a** forms reversibly from **1** and CO_2 is indicated by the following experiments. Bubbling hydrogen through a solution of **3a** (at 25 °C) sweeps CO_2 from the system and regenerates **1**.

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(6) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138–1140. In hydrocarbon solvents **1** exists as predominantly the trans isomer; however, it is in equilibrium with the cis form. In polar solvents significant (10%) quantities of the cis isomer are present at equilibrium.

(7) The complex *trans*-$PtH(O_2CH)[P(c\text{-}Hx)_3]_2$ has been shown by X-ray diffraction to be a monodentate O-bonded formato complex (ref 5). The close correspondence of the ^1H NMR parameters of this complex and those of **2** suggest an analogous structure for **2**.

(8) Anal.: % found (% calcd) C, 48.90 (48.65); H, 7.01 (7.06); P, 10.48 (10.45); Pt, 32.68 (32.92); B (by difference), 0.91 (0.93).

(9) $[HPt^A(P^AEt_3)_2(\mu\text{-}H)_2Pt^B(P^BEt_3)_2][BPh_4]$ (acetone-d_6, 30 °C): $^{31}P\{^1H\}$ NMR δ P^A 20.8 (t, $^1J(Pt^AP^A)$ = 2741, $^2J(Pt^BP^A)$ = 23 Hz), δ P^B 24.2 (t, $^1J(Pt^BP^B)$ = 2540, $^2J(Pt^AP^B)$ = 23, $^3J(P^AP^B)$ = 2.9 Hz); $^{195}Pt\{^1H\}$ NMR δ Pt^A −708, Pt^B −358 ($^1J(Pt^APt^B)$ = 866 Hz); ^1H NMR H^{term} δ −4.91 (m, $^1J(Pt^AH)$ = 1316, $^2J(Pt^BH)$ = 191 Hz), H^{bridg} δ −3.55 (m, $^1J(PtH)$ = 361, $^1J(Pt'H)$ = 592 Hz).

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