C,N-2-[(Dimethylamino)methyl]phenylplatinum Complexes Functionalized with C_{60} as Macromolecular Building Blocks

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The application of platinum(II) complexes based on the *N,N*-dimethylbenzylamine ligand (abbreviated as H−C,N) in macromolecular synthesis was demonstrated. Two cationic C,N−platinum moieties were linked with a 4,4′-bipyridine bridge, giving [{$C_6H_4(CH_2NMe_2)$-2-Pt-(PPh_3)}$_2$(4,4′-bpy)](BF_4)$_2$ (**2**), the crystal structure of which was determined. To introduce C_{60} groups into this assembly, [1,2]-methanofullerene-substituted H−C,N ligands were prepared and platinated using *cis*-$PtCl_2(DMSO)_2$. Application of the methanofullerene C,N−platinum complexes in the preparation of macrostructures afforded insoluble compounds. Therefore, phosphine ligands containing perfluoroalkyl groups were introduced into the fullerene-based complexes via a ligand exchange reaction. These fluorous complexes showed enhanced solubility in organic and fluorinated solvents. A soluble bismethanofullerene C,N−platinum(II) structure with a 4,4′-bipyridine bridge was obtained using these fluorinated fullerenes.

Introduction

The preparation of macro- and supramolecular assemblies is currently a major challenge in synthetic chemistry.[1] In particular, the use of metal centers in these structures has become a topic of increasing interest. Various organometallic compounds have been reported in which ligand systems and metals are arranged in, for example, molecular squares and cubes.[2] The introduction of special properties in these macromolecular assemblies may be accomplished by ligand modification. For example, the most abundant member in the fullerene family, C_{60}, has been incorporated in new materials as electroactive compound by attaching the C_{60} moiety to ligand frameworks.[3,4] For this reason, the design of building blocks containing fullerenes suitable for macromolecular chemistry is a rising topic in fullerene research. Up to now, C_{60} has been incorporated in photo- and electroactive diads, core and periphery C_{60}-functionalized dendritic structures, Langmuir−Blodgett films, and polymers.[3−5] In addition, specific combinations of C_{60} derivatives and transition metals have been reported in the design of new nanosized materials. An ethynyl methanofullerene has been used as a stopper molecule in a copper-containing rotaxane.[6] This system shows energy transfer from the organometallic entity to the fullerene attendant upon photoexcitation of the copper complex.[7] Using chelating transition metals, fullerene derivatives containing nitrogen donor ligands have also been assembled. Diederich and co-workers have reported the solid state structure of a bisplatinum cyclophane complex containing two pyridyl-substituted fullerene moieties,[8] and Müllen et al. have prepared the noncovalent bonded dimer of two bipyridyl-functionalized C_{60} compounds chelated to one copper(II) metal center.[9]

We have previously reported the synthesis of metal complexes based on monoanionic, terdentate coordinating bisaminoaryl ligands ([$C_6H_2(CH_2NMe_2)_2$-2,6-R-4]$^-$, abbreviated as NCN) attached via 1,3-dipolar diazo cycloaddition to C_{60}.[10,11] A closely related arene ligand,

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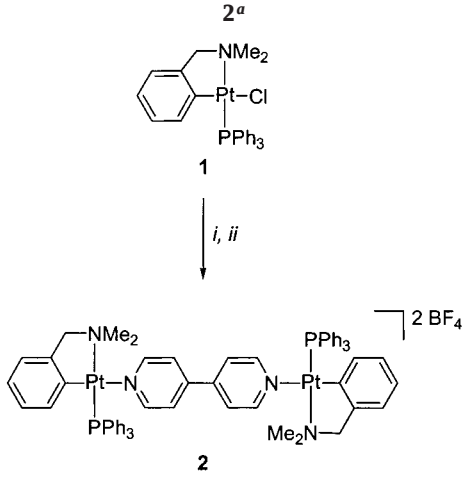
Scheme 1. Formation of DMBA−Platinum Dimer



[a] Reagents and conditions: (i) $AgBF_4$, CH_2Cl_2/acetone; (ii) 0.5 equiv 4,4′-bpy, CH_2Cl_2.

N,N′-dimethylbenzylamine (abbreviated as H−C,N), might be another excellent candidate for incorporation into macromolecular synthesis. Not only can it be cycloplatinated under relatively mild conditions using platinum(II) salts,[12] but facile ligand modification also allows the connection of H−C,N to various types of dendrimers.[13] Since the C,N anion is a potentially *C,N*-bidentate ligand, two remaining sites of the square pyramidal platinum center are potentially available for the introduction of functionalities or as a building site for enlargement of the complex. Herein, we describe this application of C,N−platinum(II) complexes in the formation of macromolecular structures. The incorporation of C_{60} in these structures via attachment of C_{60} to the H−C,N ligand has been studied in more detail. The effects on the solubility of the C,N−platinum complexes upon the attachment of C_{60} and the introduction of fluorinated alkyl groups are also presented.

Results and Discussion

The C,N−platinum(II) complex **1** was applied in the synthesis of the bisplatinum structure **2** (Scheme 1). The chloride ligand of **1** was abstracted using $AgBF_4$ in wet acetone, yielding the corresponding cationic aqua complex in situ. Subsequently, 0.5 equiv of 4,4′-bipyridine (4,4′-bpy) was added, whereupon the bridged bisplatinum complex **2** was formed. The synthesis of **2** was confirmed by multinuclear NMR spectroscopy, elemental analysis, and X-ray crystal structure determination (see below). In comparison with **1**, the resonance for the benzylic protons in the ^{1}H NMR spectrum of **2** (acetone-d_6) shifted downfield (from 4.14 to 4.35 ppm), and the signal for the NMe_2 group is shifted to higher field (from 2.92 to 2.76 ppm), both with retention of the characteristic platinum and phosphorus coupling patterns. The two observed multiplets for the PPh_3 ligand in **1** were split into three separate multiplets for the *ortho, meta*, and *para* protons in the NMR spectrum of **2**. Moreover, two new doublet resonances (δ = 8.85 and 7.63) were observed for the bridging 4,4′-bpy ligand. In this type of platinum complex, the PPh_3 ligand can be used as a spectroscopic probe for the ligands surrounding the platinum center. The $^{31}P\{^1H\}$ NMR spectrum of **2** (acetone-d_6) revealed a singlet resonance at 21.9 ppm with platinum satellites (^1J(Pt−P) = 4106 Hz). The phosphorus−platinum coupling decreased somewhat relative to that of **1** (^1J(Pt−P) = 4267 Hz, acetone-d_6), which, together with the platinum and phosphorus coupling on the protons of the dimethylamino donor arm in the ^{1}H NMR spectrum, is typical for a *trans* NMe_2−Pt−PPh_3 moiety.

Solid State Structure of 2. Crystals of complex **2** were obtained by slow diffusion of Et_2O in a concentrated solution of **2** in $CHCl_3$. A molecular plot of the structure is given in Figure 1. Table 1 shows a selection of bond lengths and bond angles for **2**, and the crystallographic details can be found in the Experimental Section. Both platinum centers of **2** display a square planar coordination mode, which is significantly distorted. The two C−N bite angles of the C,N ligand to the platinum centers are essentially the same, 81.65(15)° for Pt(1) and 82.30(16)° for Pt(2). As was suggested from NMR solution studies, the PPh_3 ligands are positioned *trans* to the NMe_2 group, which automatically positions the nitrogen donor atom of 4,4′-bpy *trans* to the aryl ring of the C,N ligand. The interplanar angle between the two pyridyl moieties is 82.6(2)°, while the torsion angle for C(20)−C(21)−C(26)−C(25) is 85.9(6)°, which shows that the two pyridyl rings of the 4,4′-bpy ligand are almost perpendicular to each other, as was shown in other examples of metal 4,4′-bpy complexes.[14]

Synthesis of Methanofullerene H−C,N Ligands. The structural arrangement of the C,N and PPh_3 ligands around the platinum center had not been changed during the synthesis of **2**. Therefore, the use of these types of complexes as building blocks seems to be a promising starting point for the synthesis of larger organometallic structures. To add a fullerene functionality to these systems, we developed a methodology for the preparation of methanofullerene H−C,N ligands. We targeted the synthesis of these systems containing one or two chelating C,N moieties per fullerene unit, which, in turn, allows the introduction of one or two metal centers per C_{60} unit. For the synthesis of potentially monometallic complexes, *N,N′*-dimethylbenzylamine was substituted at the 4-position (Scheme 2). Lithiation of 4-bromo-*N,N′*-dimethylbenzylamine (**3**) with 2 equiv of *t*-BuLi in diethyl ether at −78 °C, followed by reaction with DMF and aqueous workup, afforded benzaldehyde **4** in 86% yield. The 4-acetyl-functionalized DMBA-H compound **5** was synthesized starting from 4-methyl-

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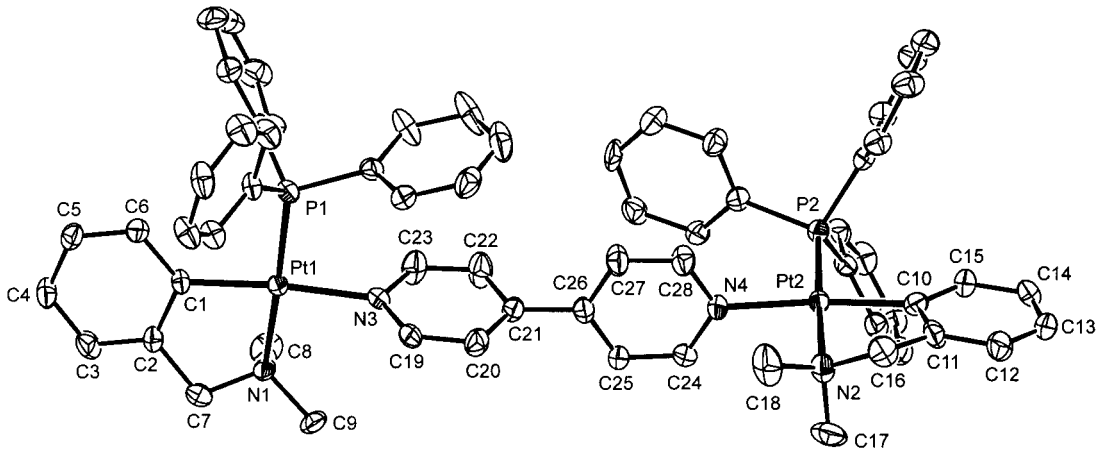
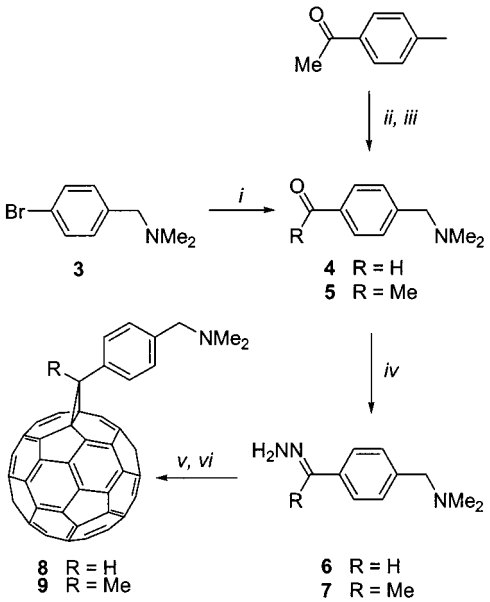


Figure 1. Displacement ellipsoid plot (50% probability level) of the molecular structure of $[C_6H_4(CH_2NMe_2)(Pt\{PPh_3\})-2]_2(4,4'\text{-bpy})\cdot 2BF_4$, **2**, with the adopted numbering scheme. The BF_4 anions, the hydrogen atoms, and the disordered solvent molecules have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 2

Pt1−N1	2.143(3)	Pt2−N2	2.139(4)
Pt1−N3	2.105(3)	Pt2−N4	2.103(3)
Pt1−P1	2.2445(11)	Pt2−P2	2.2371(11)
Pt1−C1	2.017(4)	Pt2−C10	2.019(4)
N1−Pt1−N3	90.68(13)	N2−Pt2−N4	90.13(14)
N3−Pt1−P1	91.52(9)	N4−Pt2−P2	91.58(10)
P1−Pt1−C1	96.02(12)	P2−Pt2−C10	95.98(13)
C1−Pt1−N1	81.65(15)	C10−Pt2−N2	82.30(16)
N1−Pt1−P1	174.93(10)	N2−Pt2−P2	178.11(11)
N3−Pt1−C1	172.23(14)	N4−Pt2−C10	172.43(16)
C21−C26	1.474(6)	C20−C21−C26−C25	85.9(6)

Scheme 2. Synthesis of 8 and 9[a]



[a] Reagents and conditions: (i) 2 equiv. *t*-BuLi, Et_2O, −78 °C; then DMF; (ii) NBS, CCl_4, *hν*, 80 °C; (iii) $HNMe_2$, Et_2O, 0 °C; (iv) $N_2H_4\cdot H_2O$, EtOH, 80 °C; (v) MnO_2, Et_2O, 20 h; then C_{60}, toluene; (vi) toluene, 110 °C, 6 days.

acetophenone via benzylic bromination with *N*-bromosuccinimide (NBS), followed by amination with $HNMe_2$. The formyl group in **4** and the acetyl functionality in **5** were converted by $N_2H_4\cdot H_2O$ to the corresponding hydrazone compounds **6** and **7**, respectively. Reaction of **6** and **7** with MnO_2 in diethyl ether yielded the corresponding diazo compounds in situ, which were added to C_{60} solutions in toluene. This resulted in mixtures of the [6,6]-methanofullerenes and [5,6]-fulleroids, which were isomerized to the [6,6]-methanofullerenes **8** and **9** by heating in toluene (110 °C) for 6 days.

The synthesis of a methanofullerene compound containing two H−C,N ligands proceeded from 4,4′-dimethylbenzophenone (Scheme 3), following the same reaction pathway used for **9**. 4,4′-Dimethylbenzophenone was brominated with NBS in CCl_4, followed by reaction with $HNMe_2$, yielding the bis-DMBA ketone **10**. This was then converted into the hydrazone compound **11** by $N_2H_4\cdot H_2O$. Reaction of **11** with MnO_2 in diethyl ether did not lead to the formation of the desired diazo compound. Complete conversion could be obtained using NiO_2 in place of MnO_2. Subsequently, the diazo compound was added to C_{60}, resulting in a mixture of [5,6]- and [6,6]-isomers, which was isomerized to [6,6]-methanofullerene **12** (toluene, 110 °C, 4 days).

The structures of **8**, **9,** and **12** were confirmed by spectral analysis via NMR and MALDI-TOF mass spectroscopy. For all ligands, the characteristic chemical shift patterns for 4-substituted DMBA-H ligands were observed by ^{1}H NMR spectroscopy. The different substituents on the carbon bridgehead of **8** and **9** were observed at 5.39 ppm (methine-H in **8**) and 2.54 ppm (CH_3 in **9**), which are expected shifts for aryl-substituted [6,6]-methanofullerenes.[10,11,15] The C_s symmetry of **8** and **9** was confirmed by the presence of 29 singlet resonances for **8** and 25 for **9** in the aromatic and fullerene region of the $^{13}C\{^1H\}$ NMR spectrum (33 resonances expected). The observation of 19 out of 20 expected resonances in the fullerene and aryl region for **12** is in full accordance with the C_{2v} symmetry of this molecule. The characteristic resonances for the sp^3-C_{60} carbons of the [1,2]-methanofullerene structures were observed at 75.6 ppm for **8**, 81.0 ppm for **9**, and 79.2 ppm for **12**, respectively. The selective formation of monoadducts was confirmed by MALDI-TOF mass spectroscopy in a 9-nitroanthracene matrix. Molecular ion fragments at *m*/*z* 867.0 (**8**), 880.6 (**9**), and 1001.6 (**12**), respectively, were observed.

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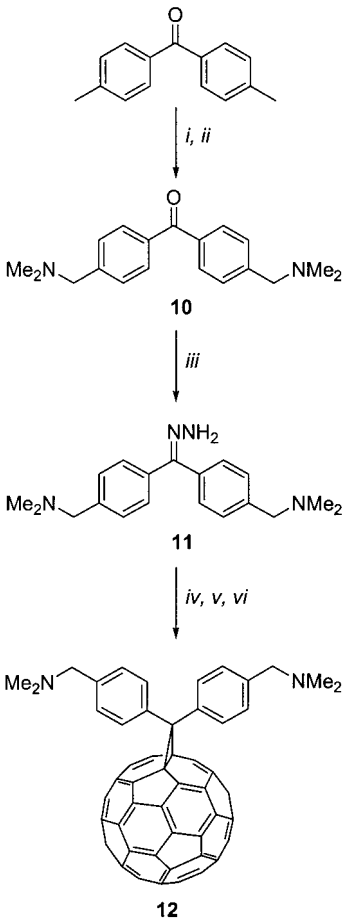
Scheme 3. Synthesis of 12[a]



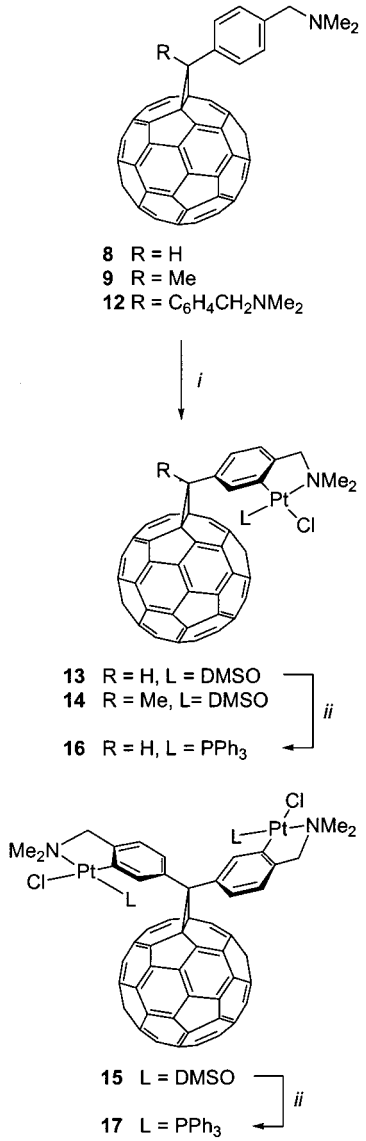
[a] Reagents and conditions: (i) NBS, CCl_4, *hν*, 65 °C; (ii) $HNMe_2$, Et_2O, 0 °C; (iii) $N_2H_4{\cdot}H_2O$, EtOH, 80 °C; (iv) NiO_2, Et_2O, 20 h; (v) C_{60}, toluene; (vi) toluene, 110 °C, 4 days.

Cycloplatination of Methanofullerene H−C,N Ligands. Direct cycloplatination of the methanofullerene H−C,N ligands was achieved by reaction of **8**, **9**, or **12** with *cis*-$PtCl_2(DMSO)_2$ in a mixture of 1,2-dichlorobenzene (ODCB) and MeOH (2:1) at 60 °C in the presence of NaOAc, resulting in the novel platinocycles (**8**)·PtCl(DMSO) (**13**), (**9**)·PtCl(DMSO) (**14**), and (**12**)·{PtCl(DMSO)}$_2$ (**15**) (Scheme 4). The presence of MeOH promotes these cycloplatination reactions. When the reaction was performed in neat ODCB only, complete conversion of **8** to **13** was not even observed after heating at 80 °C for 24 h.

^{1}H NMR analysis of **13**−**15** ($CDCl_3$, Table 2) showed the diagnostic singlet resonances with platinum couplings (47−51 Hz) for the *ortho*-aryl protons at relatively low field, an AX pattern for the other two aryl resonances, and singlets for the benzylic, DMSO, and NMe_2 groups with platinum couplings. The singlet resonances for the NMe_2 group and benzylic protons show that a fluctional process in **13**−**15** at room temperature takes place, rendering these diastereotopic groupings enantiotopic; that is, rotation about the methanofullerene−C,N bond is fast on the NMR time scale.[16] By $^{13}C\{^1H\}$ NMR measurements, 32, 31, and 21 resonances in the aryl and fullerene region (120−150 ppm) were observed for **13**, **14**, and **15**, respectively, corresponding to C_s symmetry for **13** and **14** and C_{2v} symmetry for **15**. MALDI-TOF analysis of **13** in a 9-nitroanthracene matrix showed a molecular fragment at a mass of 866.4 *m*/*z*, showing facile loss of the PtCl-DMSO moiety during the ionization proces of **13**.

(16) A similar process was observed for methanofullerene NCN complexes; see ref 11.

Scheme 4[a]



[a] Reagents and conditions: (i) $PtCl_2(DMSO)_2$, NaOAc, ODCB/MeOH (2:1), 60 °C; (ii) PPh_3, CH_2Cl_2.

Table 2. ^{1}H NMR Data[a] for Complexes 13−17

complex	H_{ortho}[b]	Ar−H[c]	CH_2N[b]	DMSO[b]	NMe_2[b]
13	8.61 (51.3)	7.69/7.24	4.10 (39.3)	3.52 (23.7)	3.01 (32.4)
14	8.58 (47.3)	7.66/7.23	4.10 (38.5)	3.48 (21.4)	3.00 (30.8)
15	8.77 (50.9)	7.84/7.15	4.02 (38.1)	3.48 (21.2)	2.95 (32.2)
16[d]	7.01 (57.0)	7.21[e]	4.18 (28.9)		3.05 (22.1)
17[d]	7.15[g]	6.75/6.22	4.23/3.98[f,g]		3.00/2.91[f]

[a] 300 MHz, $CDCl_3$, δ in ppm. [b] $J(^{195}Pt-H)$ in Hz in parentheses. [c] AX system. [d] PPh_3 resonances not included. [e] One aryl-H resonance is obscured by PPh_3 resonances. [f] $J(^{195}Pt-H)$ not resolved. [g] AB system.

The DMSO ligand in these complexes can easily be replaced by a more basic ligand.[13] Addition of PPh_3 to a CH_2Cl_2 solution of **13** or **15** led to the complete replacement of the DMSO ligand for PPh_3 at the platium center(s) within 30 min, leading to the formation of **16** and **17**, respectively. MALDI-TOF analysis of **16** and

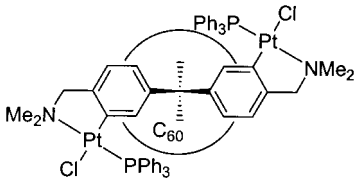


Figure 2. Top view of **17**.

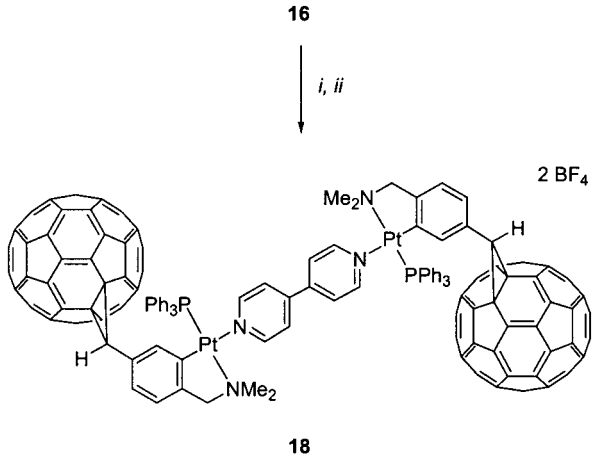
17 showed molecular fragments at $m/z = 1322.8$ (**16**) and 1949.2 (**17**), respectively, corresponding to the $[M - Cl]^+$ fragment ions. The methine proton in **16** is shifted to high field ($\Delta\delta = 0.83$) in ^{1}H NMR. In addition, characteristic phosphorus couplings were present in the benzylic and NMe_2 resonances. Interestingly, an AB system for the benzylic protons and two separate singlets for the NMe_2 groups were observed in the NMR spectrum of **17** at room temperature. Moreover, 40 resonances were visible in the fullerene and aryl region and one C_{60}-sp^3 resonance in the $^{13}C\{^1H\}$ NMR spectrum. Obviously, **17** no longer has the C_{2v} symmetry possessed by **12** and **15**. The number of observed resonances indicates that **17** has C_2 symmetry, with the two organometallic C,N−platinum complexes positioned in a "*trans*" fashion above the fullerene moiety (Figure 2). This is likely caused by the steric bulk of the PPh_3 groups, leading to a hindered rotation of the C,N−platinum moieties about the methanofullerene−C,N bonds at room temperature on the NMR time scale. The high-field shift for the C,N aryl protons is caused by the intramolecular proximity of the PPh_3 ligands to the aryl protons of the opposite C,N−platinum moiety (Table 2). Variable-temperature ^{1}H NMR spectroscopy in $Cl_2CDCDCl_2$ was performed to estimate the energy of the rotation barrier.[17] Decoalesence of the AB pattern attributed to the benzylic protons was observed at $T_c = 308$ K ($\Delta G^{\ddagger} = 62$ kJ mol^{-1}); decoalescence of the NMe_2 groups occurred at $T_c = 286$ K ($\Delta G^{\ddagger} = 61$ kJ mol^{-1}).

Macromolecular Synthesis. The platinum complexes **16** and **17** were applied in the formation of larger structures. Using the same conditions as in the synthesis of **2**, the fullerene dimer **18** was prepared from **16** with $AgBF_4$ and 4,4′-bpy in 73% isolated yield (Scheme 5). However, the isolated product was completely insoluble in common organic solvents, and the formation of the dimeric structure **18** was only shown by elemental analysis. MALDI-TOF mass spectroscopy of **18** revealed a molecular ion at $m/z = 1324.4$, which corresponds to the $[C_{60}-C,N-PtPPh_3]^+$ ion fragment of **18**. When **17** was reacted with $AgBF_4$ and 4,4′-bpy, the immediate formation of a light brown precipitate was observed, which did not dissolve in common organic solvents. This product probably consisted of polymeric methanofullerene C,N−platinum 4,4′-bpy material, but no correct elemental analysis to support this hypothesis was obtained.

Fluorinated Methanofullerene C,N−Platinum Complexes. The low solubility of fullerene macromolecules containing platinum cations has been reported by Diederich.[8] By derivatizing the C_{60} moiety with ethyl malonate groups, the solubility of their products could be enhanced, but it has been shown that such derivatization may also lead to loss of photoactivity of the C_{60} moiety.[18] Other groups have shown that the derivatization of C_{60} with fluorinated tails, for example via Diels−Alder addition, led also to increased solubility of the fullerene derivatives.[19] Our group has previously reported that the attachment of perfluoroalkyl groups onto phosphine ligands resulted in higher solubilities of the ligands and corresponding metal complexes in polar, aromatic and apolar solvents.[20,21] Therefore, we studied the use of fluorinated phosphines in the synthesis of methanofullerene C,N−platinum(II) building blocks to overcome the solubility problems encountered in this area of macromolecular synthesis. Two related perfluoroalkyl silyl substituted triphenylphosphines were reacted with **13**, affording the complexes **19** and **20** in good yield (Scheme 6). The formation of the square planar platinum phosphine complexes **19** and **20**, as depicted in Figure 3, was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. The characteristic singlet resonance was observed for both complexes at 21 ppm ($CDCl_3$) together with diagnostic Pt−P couplings (Table 3). Additional evidence for the formation of the fluorinated derivatives was obtained with MALDI-TOF mass spectroscopy. Ion fragments corresponding to the molecular fragments minus chloride were observed for both complexes.

Complexes **19** and **20** showed remarkable changes in their solubility characteristics with respect to the nonfluorinated complex **16** (Table 3). The parent methanofullerene H−C,N ligands **8** and **9** and the platinum complexes **12**−**17** are reasonably soluble in CS_2 and halogenated solvents such as CH_2Cl_2 and ODCB. Upon introduction of fluorinated tails, the complexes also dissolve moderately well in hexanes and diethyl ether.

Scheme 5. Synthesis of 18[a]



[a] Reagents and conditions: (i) $AgBF_4$, ODCB/acetone; (ii) 0.5 equiv of 4,4′-bpy, CH_2Cl_2.

(17) Variable-temperature measurements in $CDCl_3$ only showed coalescence of the NMe_2 signals ($T_c = 333$ K, $\Delta G^{\ddagger} = 70$ kJ/mol), while the fast exchange limit for the benzylic protons could not be reached.

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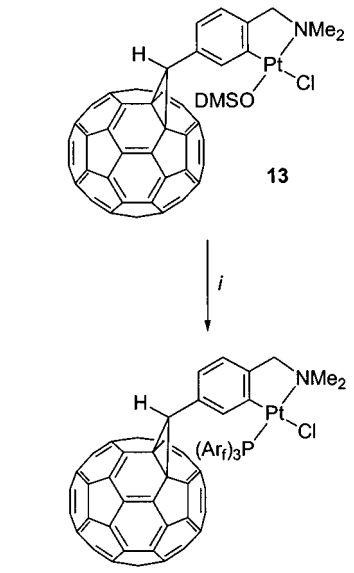
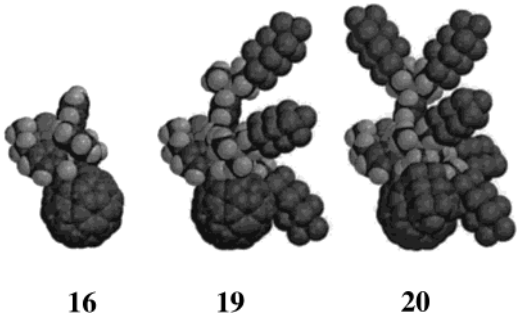
Scheme 6. Synthesis of Fluorinated Phosphine Complexes 19 and 20[a]



19 n = 1, $R_f = C_6F_{13}$
20 n = 2, $R_f = C_6F_{13}$

[a] Reagents and conditions: (i) $P(Ar_f)_3$, CH_2Cl_2.



16 **19** **20**

Figure 3. Computational structures of **16**, **19**, and **20** (MM94, Spartan 5.1.1 (SGI)).

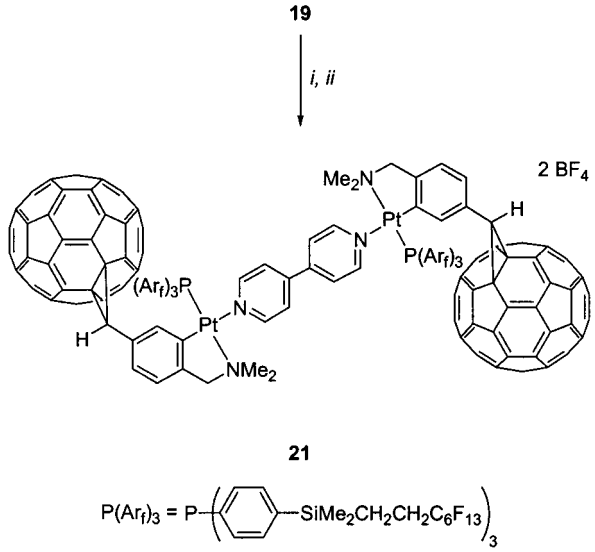
Table 3. Physical Properties for the Fullerene Platinum Phosphines 16, 19, and 20

				solubility (g L^{-1})			
complex	^{31}P NMR[a]	%F[b]	P[c]	Et_2O	hexanes	CH_2Cl_2	PFMCH
16	21.3 (4245)	0	0[d]	<0.2	<0.2	24	<0.2[d]
19	20.5 (4221)	28.8	0[d]	8.8	9.8	56	<0.2[d]
20	21.1 (4228)	41.5	0.37	99	7.2	650	4.4

[a] $CDCl_3$, δ in ppm, ^{195}Pt−P coupling in parentheses. [b] Based on the molecular formula. [c] Partition coefficient ($P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$, determined by gravimetric methods) in a toluene/PFMCH biphasic system at room temperature. [d] No material was detected in the PFMCH layer.

With an increase in the number of fluorinated tails, the solubility of **19** and **20** in diethyl ether and CH_2Cl_2 also increases. The introduction of fluorinated tails did not directly result in solubility in a fluorous solvent, such as perfluoro(methylcyclohexane) (PFMCH). Complex **19** has a low solubility in PFMCH, which is also reflected in its partition coefficient. However, complex **20**, with higher fluorous character, is soluble in PFMCH (4.4 g L^{-1}), and the partition coefficient of **20** in a toluene/PFMCH biphasic system has been found to be 0.37 at room temperature. The increase in solubility in both polar and apolar organic solvents of the platinum complexes upon increasing the number of fluorinated tails may be explained by a corresponding increase in lipophilicity of the complex.

Scheme 7. Synthesis of the Fluorinated Dimer 21[a]



[a] Reagents and conditions: (i) $AgBF_4$, CH_2Cl_2/acetone; (ii) 4,4′-bpy, CH_2Cl_2.

We chose to use **19** in the synthesis of a dimeric structure similar to **18** (Scheme 7). In contrast to **18**, the dimer **21** remained fully soluble in common organic solvents, and its formation was confirmed by NMR spectroscopy and elemental analysis. The signals for the methine, benzylic, and the NMe_2 protons all shifted to higher field ($CDCl_3$). However, all resonances were broadened, and no phosphorus or platinum couplings were distinguishable from the resonance signals in the ^{1}H NMR spectrum of **21**. The ^{195}Pt−^{31}P coupling in the ^{31}P{^{1}H} NMR spectrum decreased from 4221 Hz in **19** to 4061 Hz in **21**, which is similar to that of **2**. The UV−vis spectrum of **21** revealed absorption bands at the same wavelengths observed for **16** and **19**, namely, at 258, 328, 430, and 480 nm, commonly observed for methanofullerenes; the absorption of **21** was approximately double that of **19** due to the presence of two fullerene moieties ($\epsilon = 4.2 \times 10^4$ mol^{-1}, and $\epsilon = 7.8 \times 10^4$ mol^{-1} for **19** and **21**, respectively, at 328 nm). The UV−vis spectra of **16** and **21** are identical within experimental error, indicating that the addition of fluorinated tails does not lead to significant changes in the electronic structure of the fullerene moiety.

Conclusions

C,N−platinum complexes based on *N,N*-dimethylbenzylamine are easily prepared building blocks for macromolecular synthesis. The ligand framework is well suited for organic transformations, allowing the attachment of the *C,N*-chelating capacity to a fullerene moiety or, as demonstrated in previous work, to dendrimers. Since the C,N anion is a potentially bidentate ligand, the two remaining coordination sites at the chelated platinum center may be used as a building site for extension of the molecule or introduction of useful functionalities. In this respect, we chose to prepare a

dimeric structure based on 4,4′-bipyridine and two C,N−platinum(II) moieties. However, introduction of C_{60} in the framework of the H−C,N ligand and subsequent application in this type of macromolecular synthesis showed a large influence on the solubility of the prepared compounds. In this case, the introduction of a fluorinated phosphine ligand at the second free site of the platinum center allowed us to tune the solubility of the complexes without disturbing the nature of the C_{60} moiety. At the moment, we are extending this work toward the synthesis of larger C,N−platinum(II) structures.

Experimental Section

General Comments. All experiments were conducted under a dry dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried over appropriate materials and distilled prior to use. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 298 K (unless stated otherwise) on a Varian Inova 300 MHz or on a Varian Mercury 200 MHz NMR spectrometer. All NMR chemical shifts are in ppm referenced to residual solvent signal (^{1}H and ^{13}C{^{1}H}) or to H_3PO_4 (^{31}P{^{1}H}). The starting materials 4-[(dimethylamino)methyl]-1-bromobenzene (**3**),[22] *cis*-$PtCl_2(DMSO)_2$,[23] and the fluorinated phosphine ligands $P(C_6H_4Si(CH_3)_2C_2H_4C_6F_{13})_3$ and $P(C_6H_4Si(CH_3)(C_2H_4C_6F_{13})_2)_3$ [20] were synthesized according to literature procedures. The complex $C_6H_4(CH_2NMe_2)(PtCl\{PPh_3\})$-2 (**1**) was prepared similarly to the reported procedure for $C_6H_3(CH_2NMe_2)(SiMe_3)$-4-$(PtCl\{PPh_3\})$-2.[13d] The experimental procedures for **4**−**12** have been deposited as Supporting Information. Other chemicals were purchased from Acros and used as received. MALDI-TOF mass spectra were acquired using a Voyager-DE BioSpectrometry Workstation mass spectrometer (PerSeptive Biosystems Inc., Framingham, MA). Sample solutions were prepared in CH_2Cl_2 with an approximate concentration of 1 g L^{-1}. As the matrix, 9-nitroanthracene (9-NA) was used with approximate concentration of 40−50 g L^{-1}. An 0.5 μL aliquot of the sample solution and 0.5 μL of the matrix solution were combined on a gold MALDI target and analyzed after evaporation of the solvent. UV−vis spectra were recorded using a Varian Cary 100 UV−vis spectrophotometer in degassed CH_2Cl_2. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany).

Bis{[(dimethylamino)methyl]phenyl-2-[platina(triphenylphosphine)]}(4,4′-bipyridine)$(BF_4)_2$ (2). To a solution of **1** (1.00 g, 1.59 mmol) in CH_2Cl_2 (30 mL) was added a solution of $AgBF_4$ (0.34 g, 1.8 mmol) in wet acetone (30 mL). The reaction mixture was stirred for 2 h and filtered through Celite. To this solution was added a solution of 4,4′-bipyridine (0.12 g, 0.80 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 2 h, filtered through Celite, and evaporated in vacuo, yielding **2** as a white solid (1.09 g, 90% based on 4,4′-bipyridine). ^{1}H NMR (300 MHz, acetone-d_6): δ 8.85 (dd, ^3J = 5.2 Hz, ^4J = 1.5 Hz, 4H, bpy), 7.80−7.74 (m, 12H, PAr-H_{ortho}), 7.63 (dd, ^3J = 5.2 Hz, ^4J = 1.5 Hz, 4H, bpy), 7.54−7.49 (m, 6H, PAr-H_{para}), 7.43−7.37 (m, 12H, PAr-H_{meta}), 7.14 (d, ^3J = 6.9 Hz, 2H, Ar-H), 6.87 (td, ^3J = 7.3 Hz, ^4J = 0.9 Hz, 2H, Ar-H), 6.55 (dd, ^3J(Pt−H) = 49.6 Hz, ^3J = 8.0 Hz, ^3J(P−H) = 2.1 Hz, 2H, Ar-H), 6.38 (td, ^3J = 7.6 Hz, ^4J = 1 Hz, 2H, Ar-H), 4.18 (d, ^3J(Pt−H) = 25.8 Hz, ^4J(P−H) = 2.6 Hz, 4H, CH_2N), 3.05 (d, ^3J(Pt−H) = 25.6 Hz, ^4J(P−H) = 2.7 Hz, 12H, NCH_3). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 152.7, 148.8, 146.1, 138.9 (^1J(P−C) = 6.7 Hz), 135.2 (^2J(P−C) = 10.9 Hz), 132.9 (^2J(P−C) = 6.7 Hz), 131.7 (^4J(P−C) = 1.9 Hz), 129.1, 128.8 (^3J(P−C) = 11.5 Hz), 128.3, 125,0, 124.7, 122.2 (bpy-*C*, PAr-*C* and Ar-*C*), 72.9 (*C*H_2N), 50.2 (N*C*H_3). ^{31}P{^{1}H} NMR (81 MHz, acetone-d_6): δ 21.9 (^1J(P−Pt) = 4106 Hz). Anal. Calcd for $C_{64}H_{62}N_4B_2F_8P_2Pt_2$: C 50.81, H 4.13, N 3.70. Found: C 50.54, H 4.03, N 3.55.

1,2-Dihydro-61-(3′-[chloro(DMSO)platina]-4′-[(dimethylamino)methyl]phenyl)-1,2-methanofullerene[60] (13). To a solution of **8** (253 mg, 0.29 mmol) in 1,2-dichlorobenzene (75 mL) was added *cis*-$PtCl_2(DMSO)_2$ (0.13 g, 0.31 mmol) and a solution of NaOAc (25 mg, 0.30 mmol) in MeOH (40 mL). The reaction mixture was heated at 70 °C for 20 h, after which all volatile components were removed under reduced pressure. The remaining black solid was suspended in a mixture of CS_2/$CHCl_3$ (1:1 v/v %, 50 mL) and filtered over a G4 glass frit. All volatiles were removed, and the remaining black solid was washed with Et_2O (2 × 40 mL) and dried in vacuo, yielding **13** as a brown solid (266 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (s, ^3J(Pt−H) = 51.3 Hz, 1H, Ar-H), 7.69 (d, ^3J = 7.2 Hz, 1H, Ar-*H*), 7.23 (d, ^3J = 8.1 Hz, 1H, Ar-*H*), 5.41 (s, 1H, bridge-C*H*), 4.10 (s, ^3J(Pt−H) = 39.3 Hz, 2H, CH_2N), 3.52 (s, ^3J(Pt−H) = 23.7 Hz, 6H, SCH_3), 3.01 (s, ^3J(Pt−H) = 32.4 Hz, 6H, NCH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 150.18, 148.45, 146.34, 145.85, 145.80, 145.17, 145.13, 145.05, 144.86, 144.69, 144.65, 144.56, 144.39, 144.33, 144.07, 143.76, 143.73, 143.10, 142.98, 142.95, 142.89, 142.78, 142.40, 142.12, 141.05, 140.81, 138.37, 137.07, 136.35, 130.63, 127.55, 121.66 (C_{60}-*C* and Ar-*C*), 76.0 (C_{60}-sp^3), 74.8 (*C*H_2N), 52.4 (N*C*H_3), 46.8 (S*C*H_3) 44.1 (bridgehead-*C*). MALDI-TOF-MS (9-NA): *m*/*z* 866.4 ([M − PtCl(DMSO)]$^+$) Anal. Calcd for $C_{72}H_{18}NClOPtS$: C 73.57, H 1.54, N 1.19. Found: C 73.39, H 1.66, N 1.20.

1,2-Dihydro-61-methyl-61-(3′-[chloro(DMSO)platina]-4′-[(dimethylamino)methyl]phenyl)-1,2-methanofullerene-[60] (14). Compound **14** was synthesized similarly to the synthesis of **13**, starting from **9** (195 mg, 0.221 mmol), *cis*-$PtCl_2(DMSO)_2$ (95 mg, 0.23 mmol), and NaOAc (20 mg, 0.23 mmol), yielding **14** as a brown solid (215 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.58 (d, ^3J(Pt−H) = 47.3 Hz, ^4J = 1.5 Hz, 1H, Ar-H_{ortho}), 7.66 (dd, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 1H, Ar-*H*), 7.23 (d, ^3J = 7.6 Hz), 4.10 (s, ^3J(Pt−H) = 38.5 Hz, 2H, CH_2N), 3.48 (s, ^3J(Pt−H) = 21.4 Hz, 6H, SCH_3), 3.00 (s, ^3J(Pt−H) = 30.8 Hz, 6H, NCH_3), 2.55 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.99, 148.80, 146.44, 146.12, 145.59, 145.41, 145.36, 145.31, 145.18, 145.10, 144.95, 144.89, 144.64, 144.52, 144.09, 143.98, 143.31, 143.20, 143.13, 142.60, 142.44, 142.41, 142.35, 141.16, 140.92, 138.16, 137.65, 137.23, 137.12, 127.67, 121.83 (C_{60}-*C* and Ar-*C*), 81.6 (C_{60}-sp^3), 75.1 (^2J(Pt−C) = 46.9 Hz, *C*H_2N), 52.7 (N*C*H_3), 48.5 (bridgehead-C), 47.5 (S*C*H_3, ^3J(Pt−C) = 64.3 Hz), 22.9 (CH_3). Anal. Calcd for $C_{73}H_{20}NClOPtS$: C 73.71, H 1.69, N 1.18. Found: C 73.66, H 1.54, N 1.15.

1,2-Dihydro-61-bis(3′-[chloro(DMSO)platina]-4′-[(dimethylamino)methyl]phenyl)-1,2-methanofullerene-[60] (15). Compound **15** was synthesized similarly to the synthesis of **13**, starting from **12** (220 mg, 0.220 mmol), *cis*-$PtCl_2(DMSO)_2$ (0.19 g, 0.45 mmol), and NaOAc (39 mg, 0.48 mmol), yielding **15** as a brown solid (246 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (d, ^3J(Pt−H) = 50.9 Hz, ^4J = 1.8 Hz, 2H, Ar-H_{ortho}), 7.84 (dd, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 2H, Ar-*H*), 7.15 (d, ^3J = 7.7 Hz, 2H, Ar-H), 4.02 (s, ^3J(Pt−H) = 38.1 Hz, 4H, CH_2N), 3.48 (s, ^3J(Pt−H) = 21.2 Hz, 12H, SCH_3), 2.95 (s, ^3J(Pt−H) = 32.2 Hz, 12H, NCH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.40, 145.81, 145.71, 145.11, 144.98, 144.62, 144.53, 144.06, 143.82, 142.93, 142.90, 142.84, 142.28, 142.08, 140.73, 137.92, 137.06, 136.87, 135.99, 127.49, 121.73 (C_{60}-*C* and Ar-*C*), 79.8 (C_{60}-sp^3), 74.8 (^2J(Pt−C) = 48.5 Hz, *C*H_2N), 59.2 (bridgehead-*C*), 52.4 (N*C*H_3), 46.7 (^3J = 59.5 Hz, SO*C*H_3). Anal. Calcd for $C_{83}H_{34}N_2Cl_2O_2Pt_2S_2$: C 61.67, H 2.12, N 1.73. Found: C 61.79, H 2.10, N 1.70.

1,2-Dihydro-61-(3′-[chloro(triphenylphosphine)platina]-4′-[(dimethylamino)methyl]phenyl)-1,2-methanofullerene-

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[60] (16). To a solution of **13** (80 mg, 0.068 mmol) in CH_2Cl_2 (30 mL) was added PPh_3 (19 mg, 0.072 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 2 h and filtered over Celite, and all volatiles were removed in vacuo. The remaining black solid was washed with MeOH (40 mL) and Et_2O (2 × 40 mL) and dried in vacuo, yielding **16** as a brown solid (87 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (m, 6H, PAr-*H*), 7.39 (m, 4H, PAr and Ar-*H*), 7.31 (m, 6H, PAr-*H*), 7.21 (d, ^3J = 7.8 Hz, 1H, Ar-H), 7.01 (s, ^3J(Pt−H) = 57.0 Hz, 1H, Ar−H_{ortho}), 4.67 (s, 1H, bridge-C*H*), 4.18 (d, ^4J(P−H) = 2.7 Hz, ^3J(Pt−H) = 28.9 Hz, 2H, CH_2N), 3.05 (d, ^4J(P−H) = 2.7 Hz, ^3J(Pt−H) = 22.1 Hz, 6H, NCH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.96, 147.80, 145.46, 145.35, 145.09, 145.07, 144.97, 144.70, 144.65, 144.59, 144.47, 144.28, 144.17, 143.98, 143.64, 143.60, 142.93, 142.83, 142.64, 142.45, 142.09, 141.98, 140.85, 140.75, 139.35 (d, ^1J(P−C) = 6.1 Hz), 138.21, 136.01, 135.25 (d, ^2J(P−C) = 11.0 Hz), 130.79 (d, ^4J(P−C) = 2.1 Hz), 130.52, 129.70, 127.95 (d, ^3J(P−C) = 11.0 Hz), 125.68, 121.81 (C_{60}-*C*, PAr-*C* and Ar-*C*), 75.8 (C_{60}-sp^3), 74.2 (*C*H_2N), 50.9 (N*C*H_3), 43.6 (bridgehead-*C*). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 21.3 (^1J(P−Pt) = 4245 Hz). MALDI-TOF-MS (9-NA): *m*/*z* 1322.78 ([M − Cl]$^+$). Anal. Calcd for $C_{88}H_{27}NClPtP$: C 77.74, H 2.00, N 1.03. Found: C 77.46, H 1.96, N 0.98.

1,2-Dihydro-61-bis(3′-[chloro(triphenylphosphine)platina]-4′-[(dimethylamino)methyl]phenyl)-1,2-methanofullerene[60] (17). Compound **17** was synthesized using a procedure similar to that for compound **16**, starting from **15** (116 mg, 0.072 mmol) and PPh_3 (40 mg, 0.15 mmol), yielding **17** as a brown solid (132 mg, 93%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.65−7.58 (m, 12H, PAr-*H*), 7.40−7.27 (m, 18H, PAr-*H*), 7.15 (s, 2H, 1H, Ar-H_{ortho}), 6.75 (d, ^3J = 7.8 Hz, 2H, Ar-H), 6.23 (d, ^3J = 6.9 Hz, 2H, Ar-H), 4.22/3.99 (d, AB, *J*(AB) = 12.9 Hz, 4H, CH_2N), 3.00, 2.92 (2 × s, 12H, NCH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 148.69, 148.56, 146.33, 145.37, 145.22, 145.13, 145.05, 144.96, 144.83, 144.60, 144.54, 144.52, 144.43, 144.00, 143.89, 143.63, 143.69, 143.44, 142.79, 142.58, 142.48, 142.31, 142.13, 142.07, 141.98, 141.96, 140.28, 140.19, 137.95 (d, ^1J(P−C) = 6.8 Hz), 137.69, 137.43, 136.78, 136.68, 136.12 (d, ^2J(P−C) = 2.2 Hz), 135.05 (d, ^2J(P−C) = 11.2 Hz), 131.05, 130.73 (d, ^4J(P−C) = 2.1 Hz), 128.05 (d, ^3J(P−C)= 11.1 Hz), 125.79, 121.80 (C_{60}-*C*, PAr-*C*, and Ar-*C*), 79.4 (C_{60}-sp^3), 74.3 (*C*H_2N), 58.4 (bridgehead-*C*), 51.2, 50.4 (N*C*H_3). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 21.1 (^1J(P−Pt) = 4275 Hz). MALDI-TOF-MS (9-NA): *m*/*z* 1949.2 ([M − Cl]$^+$). Anal. Calcd for $C_{115}H_{52}N_2Cl_2P_2Pt_2$: C 69.60, H 2.64, N 1.41. Found: C 69.73, H 2.56, N 1.43.

Bis{1,2-dihydro-61-(3′-[platina(triphenylphosphine)]-4′-[(dimethylamino)methyl]phenyl)-1,2-methanofullerene-[60]}(4,4′-bipyridine)$(BF_4)_2$ (18). To a solution of **16** (280 mg, 0.206 mmol) in 1,2-dichlorobenzene (40 mL) was added a solution of $AgBF_4$ (44 mg, 0.23 mmol) in acetone (25 mL). The reaction mixture was stirred for 1 h, concentrated in vacuo to a volume of 30 mL, and filtered through Celite. A solution of 4,4′-bipyridine (16 mg, 0.102 mmol) in CH_2Cl_2 (10 mL) was added and the reaction mixture stirred overnight, whereupon a brown precipitate was formed. The precipitate was isolated by centrifugation/decantation, washed with CH_2Cl_2 (40 mL) and acetone (40 mL), and dried in vacuo, yielding **18** as a brown solid (221 mg, 73% based on 4,4′-bipyridine). The product was too insoluble for NMR analysis. MALDI-TOF-MS (9-NA): *m*/*z* 1324.4 (mass corresponds to [**16** − Cl]$^+$). Anal. Calcd for $C_{186}H_{62}B_2F_8N_4P_2Pt_2$: C 75.01, H 2.10, N 1.88. Found: C 74.87, H 1.98, N 1.84.

1,2-Dihydro-61-(3′-[chloro(tris[4-{(2-(perfluorohexyl)-ethyl)dimethylsilyl}phenyl]phosphine)platina]-4′-[(dimethylamino)methyl]phenyl)-1,2-methanofullerene-[60] (19). To a solution of **13** (55 mg, 0.046 mmol) in degassed CH_2Cl_2 (30 mL) was added the fluorinated phosphine P(C_6H_4-Si$(CH_3)_2C_2H_4C_6F_{13})_3$ (64 mg, 0.044 mmol). The reaction mixture was stirred for 2 h, and all volatile components were evaporated in vacuo. The crude product was suspended in Et_2O and chromatographed over silica gel, using Et_2O as eluents. Evaporation of the first eluted fraction yielded **19** as a brown solid (82 mg, 69%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.68 (m, 6H, PAr-*H*), 7.45 (m, 7H, PAr-*H* and Ar-*H*), 6.95 (s, 1H, Ar-H_{ortho}), 5.00 (s, 1H, bridge-C*H*), 4.16 (s, 2H, CH_2N), 3.02 (s, 6H, NCH_3), 1.97 (m, 6H, CH_2CF_2), 0.90 (m, 6H, SiCH_2), 0.29 (s, 18H, SiCH_3).^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.78, 147.93, 147.81, 145.49, 145.16, 145.05, 145.03, 144.75, 144.68, 144.42, 144.37, 144.22, 143.97, 143.69, 143.54, 143.06, 142.96, 142.93, 142.66, 142.42, 142.06, 142.00, 140.90, 140.71, 140.69, 140.60, 139.81, 139.74, 138.19, 137.79 (d, ^4J(P−C) = 6.7 Hz), 136.01, 134.50 (d, ^2J(P−C) = 10.3 Hz), 133.08 (d, ^3J(P−C) = 11.0 Hz), 131.45, 130.64, 129.29 (d, ^2J(P−C) = 1.8 Hz), 125.75, 122.18 (C_{60}-*C*, PAr-*C*, and Ar-*C*), 122−105 (m, *C*F_2 and *C*F_3), 75.4 (C_{60}-sp^3), 74.3 (*C*H_2N), 50.9 (N*C*H_3), 43.6 (bridgehead-*C*), 25.8 (^2J(C−F) = 23.6 Hz, *C*H_2CF_2), 5.2 (Si*C*H_2), −3.7 (Si*C*H_3). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 20.5 (^1J(P−Pt) = 4221 Hz). MALDI-TOF-MS (9-NA): *m*/*z* 2572.5 ([M − Cl]$^+$). Anal. Calcd for $C_{118}H_{54}NClF_{39}PPtSi_3$: C 55.10, H 2.12, N 0.54. Found: C 55.19, H 1.98, N 0.58.

1,2-Dihydro-61-(3′-[chloro(tris[4-{bis(2-(perfluorohexyl)-ethyl)methylsilyl}phenyl]phosphine)platina]-4′-[(dimethylamino)methyl]phenyl)-1,2-methanofullerene[60] (20). Compound **20** was synthesized similarly to the synthesis of **19**, starting from **13** (49 mg, 0.042 mmol) and fluorinated phosphine P$(C_6H_4Si(CH_3)(C_2H_4C_6F_{13})_2)_3$ (98 mg, 0.040 mmol), yielding **20** as a brown solid (114 mg, 76%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.68 (m, 6H, PAr-*H*), 7.45 (m, 7H, PAr-*H* and Ar-*H*), 7.28 (d, ^3J = 7.8 Hz, 1H, Ar-*H*), 6.98 (s, 1H, Ar-H_{ortho}), 4.57 (s, 1H, bridge-C*H*), 4.18 (s, 2H, CH_2N), 3.03 (s, 6H, NCH_3), 1.98 (m, 12H, CH_2CF_2), 1.04 (m, 12H, SiCH_2), 0.34 (s, 9H, SiCH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 149.55, 147.99, 147.73, 145.49, 145.32, 145.22, 145.11, 145.07, 144.75, 144.72, 144.69, 144.41, 144.32, 144.24, 143.91, 143.70, 143.45, 143.13, 143.08, 143.03, 143.00, 142.97, 142.89, 142.67, 142.36, 142.08, 141.95, 140.95, 140.55, 139.50, 139.43, 138.17, 138.05, 137.66 (d, ^4J(P−C) = 6.7 Hz), 136.02, 134.79 (d, ^2J(P−C) = 10.3 Hz), 133.45, 133.22 (d, ^3J(P−C) = 10.3 Hz), 132.22, 131.42, 129.38 (d, ^2J(P−C) = 1.8 Hz), 126.02, 122.65 (C_{60}-*C*, PAr-*C*, and Ar-*C*), 122−105 (m, *C*F_2 and *C*F_3), 76.6 (C_{60}-sp^3), 74.4 (*C*H_2N), 51.0 (N*C*H_3), 43.4 (bridgehead-*C*), 25.6 (^2J(C−F) = 23.7 Hz, *C*H_2-CF_2), 3.3 (Si*C*H_2), −6.3 (Si*C*H_3). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 21.1 (s, ^1J(P−Pt) = 4228 Hz). MALDI-TOF-MS (9-NA): *m*/*z* 3532.8 ([M − Cl]$^+$). Anal. Calcd for $C_{139}H_{57}NClF_{78}$-$PPtSi_3$: C 46.78, H 1.61, N 0.39. Found: C 46.85, H 1.76, N 0.45.

Bis{1,2-dihydro-61-(3′-[platina(tris[4-{(2-(perfluorohexyl)-ethyl)dimethylsilyl}phenyl]phosphine)]-4′-[(dimethylamino)-methyl]phenyl)-1,2-methanofullerene[60]}(4,4′-bipyridine)-$(BF_4)_2$ (21). To a solution of **19** (41 mg, 0.015 mmol) in CH_2-Cl_2 (25 mL) was added 1.0 mL of a 18 mM solution of $AgBF_4$ in acetone (3.4 g L^{-1}). The reaction mixture was stirred for 2 h, and 1.0 mL of a 8 mM solution of 4,4′-bpy in CH_2Cl_2 (1.3 g L^{-1}) was added. The reaction mixture was stirred for 2 h, filtered through Celite, and evaporated to dryness. The crude product was washed with MeOH (25 mL) and Et_2O (10 mL) and dried in vacuo, yielding **21** as a dark brown solid (37 mg, 85% based on 4,4′-bipyridine). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.53−7.26 (m, 6H, PAr-*H*), 6.95 (s, 1H, Ar-H_{ortho}), 4.55 (s, 3H, bridge-C*H*), 4.27 (s, 4H, CH_2N), 3.62 (s, 12H, NCH_3), 1.97 (m, 6H, CH_2CF_2), 0.98−0.89 (m, 6H, SiCH_2), 0.21 (s, 36H, SiCH_3). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 20.0 (s, ^1J(P−Pt) = 4061.6 Hz). Anal. Calcd for $C_{246}H_{116}B_2F_{86}N_4P_2Pt_2Si_6$: C 54.68, H 2.16, N 1.04. Found: C 54.60, H 2.24, N 1.10.

Determination of Partition Coefficients and Solubilty Data. Partition coefficients were determined by dissolving 10 μmol of complex **16**, **19**, or **20** in toluene (2.00 mL), after which perfluoro(methylcyclohexane) (2.00 mL) was added. The mixture was stirred thoroughly for 5 h at room temperature. When two clear layers were obtained, an aliquot (1.00 mL) was removed from each layer by syringe. This was evaporated in

vacuo and kept under vacuum for 20 h. Then the weight of the residue was determined. For solubility determination, an 250 μL aliquot was taken from a saturated solution of **16**, **19**, or **20** in 1.00 mL of solvent, evaporated in vacuo, and kept under vacuum for 20 h. Then the weight of the residue was determined.

Crystal Structure Determination of 2. $[C_{64}H_{62}N_4P_2Pt_2](BF_4)_2$ + solvent, fw = 1512.92,[24] colorless needle, 0.45 × 0.03 × 0.03 mm^3, triclinic, $P\bar{1}$, a = 9.5341(1) Å, b =18.7097(2) Å, c = 22.0895 Å, α = 110.1881(5)°, β = 98.5576(4), γ = 100.5523(7)°, V = 3538.44(7) Å^3, Z = 2, ρ = 1.42 g cm^{-3},[24] 52 416 measured reflections, 15 898 unique reflections (R_{int} = 0.069). Intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (Mo Kα, λ = 0.71073 Å) at a temperature of 150 K. Absorption correction with the program PLATON[25] (routine DELABS, μ = 4.05 mm^{-1},[24] 0.42−0.81 transmission). The structure was solved with automated Patterson methods with the program DIRDIF97[26] and refined with the program SHELXL97[27] against F^2 of all reflections up to a resolution of $(\sin \vartheta/\lambda)_{max}$ = 0.65 Å^{-1}. Non hydrogen atoms were refined freely with anisotropic displacement parameters, and hydrogen atoms were refined as rigid groups. The crystal structure contains voids (787.5 Å^3/unit cell) filled with disordered chloroform solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation (program PLATON,[25] CALC SQUEEZE, 237 e$^-$/unit cell). R ($I > 2\sigma(I)$): R1 = 0.0359, wR2 = 0.0745. R (all data): R1 = 0.0576, wR2 = 0.0785. S = 1.002. The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON.[25]

(24) Derived values do not contain the contribution of the disordered solvent.

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Supporting Information Available: The experimental procedures for **4**−**12**, details of the X-ray crystal structure analysis of complex **2**, MALDI-TOF spectra of **21** and **22**, and a picture concerning the FBS experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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