Organometallics **1994,** *13,* 3651-3656 3651

η^3-Trimethylenemethane Complex of Platinum

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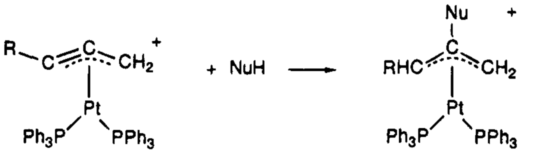
Received April 15, 1994®

The first trimethylenemethane complex of platinum, $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHPh)$ (**1**), was synthesized from $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]O_3SCF_3$ and $Na[CH(CO_2Me)_2]$. Its structure shows η^3 bonding of the trimethylenemethane ligand to platinum, with a fold angle of 59.9° between the planes C—Pt—C and coordinated C—C—C. **1** undergoes protonation at the $C(CO_2Me)_2$ methylene carbon atom to yield $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(CH(CO_2Me)_2)CHPh)]^+$ and [3 + 2] cycloaddition of tetracyanoethylene to the organic ligand to afford a platinum–olefin complex, $(PPh_3)_2Pt(PhCH{=}\overline{CCH_2C(CN)_2C(CN)_2C}(CO_2Me)_2)$.

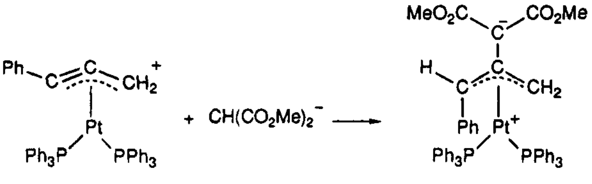
Introduction

Since the report of $(CO)_3Fe(\eta^4\text{-}CH_2C(CH_2)CH_2)$ in 1966 by Emerson and co-workers,[1] transition-metal trimethylenemethane complexes have received considerable attention.[2] Envisioned as a method of stabilization of a fragment otherwise unisolable, the formation of these complexes has sparked theoretical, structural, and, especially, synthetic interests. Interest in synthesis stems from the observations that some trimethylenemethane complexes participate in [3 + 2] cycloaddition reactions with unsaturated compounds.[2b-e]

We[3,4] and others[5] have recently prepared novel η^3-propargyl/allenyl complexes of platinum, $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCR)]^+$ (R = H, Ph), which react with a series of nucleophiles NuH (NuH = OR, NHR, NR_2, SR, inter alia) to afford heteroatom-substituted η^3-allyl complexes (eq 1). We find[3] that a similar reaction between $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ and $Na[CH(CO_2Me)_2]$ leads to the formation and isolation of a zwitterionic trimethylenemethane[6] complex of platinum, $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHPh)$ (**1**) (eq 2). This product is of considerable interest because analogous, but elusive,[7] palladium trimethylenemethane complexes have been implicated in cycloaddition reactions involving electron-deficient alkenes.[8]



(1)



(2)

1

In this paper, we describe in detail the previously communicated[3] synthesis of **1**. In addition, we report an X-ray diffraction study and preliminary reaction chemistry of this η^3-trimethylenemethane complex.

Experimental Section

General Procedures. All reactions and sample manipulations were carried out under an atmosphere of dry Ar by use of standard procedures.[9] Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Infrared, NMR (^1H, ^{13}C, and ^{31}P), and mass spectra (EI) were obtained as previously described.[10]

Materials. Solvents were purified by distillation under an Ar atmosphere according to literature procedures.[11] Reagents were obtained from commercial sources and used as received, except as noted below. Commercially available tetracyanoethylene (TCNE) was purified by sublimation. $[NEt_3H]BPh_4$ was obtained by a metathesis reaction of $[NEt_3H]Cl$ with $NaBPh_4$ in H_2O. The η^3-propargyl/allenyl complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]O_3SCF_3$ was prepared as previously described.[3]

Preparation of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHPh)$ (1). The reaction must be performed under scrupulously dry conditions, since $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]O_3SCF_3$ reacts with H_2O.[4] Solid $Na[CH(CO_2Me)_2]$ (0.153 g, 0.996 mmol), obtained

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® Abstract published in *Advance ACS Abstracts,* August 1, 1994.

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[6] In this paper, trimethylenemethane metal complexes are referred to in a broad context and include complexes with derivatized trimethylenemethane ligands, such as $CH_2C(C(CO_2Me)_2)CHPh$.

[7] However, during the preparation of this manuscript we were informed by Professor J.-T. Chen that he and co-workers prepared and characterized by X-ray crystallography the η^3-trimethylenemethane complex of palladium $(PPh_3)_2Pd(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CH_2)$ and studied its cycloaddition reactions. Note Added in Proof. This work has now been published; see: Su, C.-C.; Chen, J.-T.; Lee, G.-S.; Wang, Y. *J. Am. Chem. Soc.* **1994,** *116,* 4999.

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from $CH_2(CO_2Me)_2$ and NaH, was treated with a solution of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]O_3SCF_3$ (0.980 g, 0.996 mmol), in 100 mL of CH_2Cl_2. Almost immediately the color of the solution turned from yellow-green to orange. The solution was stirred for 1 h at room temperature, and the solvent was removed under reduced pressure. The solid residue was extracted with ca. 20 mL of benzene, the extract was filtered, and the filtrate was concentrated to ca. 5 mL. Addition of 100 mL of hexanes induced the precipitation of **1**. The yellow solid was washed with hexanes and dried under vacuum for 1 day. Yield: 0.800 g (83%). ^1H NMR (CD_2Cl_2): δ 7.5−7.0 (m, 35 H, Ph), 5.38 (m, 1 H, C*H*Ph), 4.00 (m, 1 H, H_{syn}), 3.49 (s, 6 H, Me), 2.60 (dd, 1 H, $J_{PH} = 11.3$ Hz, $^2J_{HH} = 4.2$ Hz, $J_{PtH} = 55$ Hz, H_{anti}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 170.7 (s, CO_2Me), 149.2 (t, $J_{PC} = 3.4$ Hz, $J_{PtC} = 91$ Hz, H_2CC), 144−122 (m, Ph), 88.4 (s, *C*($CO_2Me)_2$), 70.7 (d, $J_{PC} = 47$ Hz, $J_{PtC} = 227$ Hz, *C*HPh), 50.3 (s, Me), 46.6 (d, $J_{PC} = 42$ Hz, $J_{PtC} = 159$ Hz, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 20.1 (d, $J_{PP} = 3.6$ Hz, $J_{PtP} = 3359$ Hz), 18.6 (d, $J_{PtP} = 3126$ Hz). Anal. Calcd for $C_{50}H_{44}O_4P_2Pt$: C, 62.17; H, 4.59. Found: C, 61.97; H, 4.79.

Protonation of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHPh)$ (1). A solution of $[NEt_3H]BPh_4$ (0.062 g, 0.146 mmol) in 20 mL of THF was added to a stirred yellow solution of **1** (0.141 g, 0.146 mmol) in 10 mL of THF. The resulting colorless solution was stirred for 10 min before all solvent was removed under vacuum. To the solid residue was added 20 mL of hexanes, and the mixture was stirred for 1 h. The white solid was collected on a filter frit and dried under vacuum for 2 days. Yield of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(CH(CO_2Me)_2)CHPh)]BPh_4$ (**2**): 0.188 g (87%). ^1H NMR (CD_2Cl_2): δ 7.5−6.7 (m, 35 H, Ph), 5.59 (m, 1 H, C*H*Ph), 4.11 (s, 1 H, $J_{PtH} = 15$ Hz, CH), 3.82 (s, 3 H, Me), 3.80 (m, 1 H, H_{syn}), 3.74 (s, 3 H, Me), 3.10 (m, 1 H, H_{anti}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 166.4 (s, $J_{PtC} = 21$ Hz, *C*O_2Me), 166.3 (s, $J_{PtC} = 18$ Hz, *C*O_2Me), 164.4 (q, $^1J_{C^{11}B} = 49$ Hz; septet, $^1J_{C^{10}B} = 16$ Hz, ipso C of BPh_4), 137−122 (m, Ph), 117.3 (t, $J_{PC} = 1.8$ Hz, $J_{PtC} = 32$ Hz, H_2CC), 91.6 (d, $J_{PC} = 25$ Hz, $J_{PtC} = 76$ Hz, *C*HPh), 63.1 (d, $J_{PC} = 29$ Hz, $J_{PtC} = 88$ Hz, CH_2), 58.8 (s, $J_{PtC} = 25$ Hz, *C*H($CO_2Me)_2$), 54.0 (s, slightly br, Me). Assignments were assisted by a ^{13}C DEPT spectrum. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 14.7 (d, $J_{PP} = 13$ Hz, $J_{PtP} = 3965$ Hz), 14.3 (d, $J_{PtP} = 3834$ Hz). Anal. Calcd for $C_{74}H_{65}BO_4P_2Pt$: C, 69.10; H, 5.09. Found: C, 68.87; H, 5.06.

Reaction of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHPh)$ (1) with Tetracyanoethylene (TCNE). Freshly sublimed TCNE (0.014 g, 0.109 mmol) and **1** (0.200 g, 0.207 mmol) were added to 5 mL of benzene in a flask protected from light with aluminum foil. The contents were stirred for 1.5 h at room temperature to produce a deep orange solution and a small amount of an insoluble material. The mixture was filtered, the filtrate was evaporated to dryness, and the residue was extracted twice with 10-mL portions of 1:1 (v/v) benzene/hexanes. The extracts were combined, and solvent was removed under reduced pressure. Recrystallization from 0.25 mL of CH_2Cl_2 and 10 mL of Et_2O afforded a yellow solid, **3**, which was dried under vacuum for 2 days. Yield: 0.067 g (56%). IR (C_6H_6): ν(CN) 2196, ν(CO) 1704, ν(C=C), Ph 1600, 1481, 1435 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.0−7.0 (m, 35 H, Ph), 6.19 (d, 1 H, $J_{PH} = 8.7$ Hz, $J_{PtH} = 22$ Hz, =C*H*Ph), 3.68 (s, 3 H, CO_2Me), 3.04 (d, br, 1 H, $^2J_{HH} = 15$ Hz, C*H*H), 2.52 (s, 3 H, CO_2Me), 2.16 (m, 1 H, $^2J_{HH} \sim 12$ Hz, $J_{PH} = 12$ Hz, $J_{PtH} \sim 40$ Hz, CH*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.5 (m, *C*O_2Me), 170 (m, *C*O_2Me), 140−127 (m, Ph), 111.9 (s, CN), 111.4 (s, CN), 110.7 (s, 2 CN), 57.0 (dd, $J_{PC} = 57$, 3.4 Hz, *C*HPh), 55.3 (d, *C*($CO_2Me)_2$), 51.9 (s, CO_2*Me*), 50.1 (s, CO_2*Me*), 44.7 (d, *C*($CN)_2$), 44.5 (d, *C*($CN)_2$), 43.8 (d, $J_{PC} = 47$ Hz, CH_2.) $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.9 (d, $J_{PP} = 22.2$ Hz, $J_{PtP} = 3930$ Hz), 21.1 (d, $J_{PtP} = 3430$ Hz). Anal. Calcd for $C_{56}H_{44}N_4O_4P_2Pt$: C, 61.48; H, 4.05; N, 5.12. Found: C, 61.31; H, 4.21; N, 4.99.

Structure Determination of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(C(CO_2Me)_2)CHPh)$ ($(1)_2\cdot PhMe\cdot {}^1/_2THF$). Crystals were grown by slow evaporation of solvent from a saturated solution of **1** (prepared in THF solution) in CH_2Cl_2/toluene. The data-collection crystal was a yellow pyramidally-shaped piece which had been cut from a larger crystal. As a check of crystal stability, six standard reflections were measured after every 150 reflections during data collection. Their intensities decreased slightly, with the average change in intensity being 3.2%. Data processing was done with the TEXSAN software package.[12] A linear decay correction was applied to the data.

Table 1. Crystal Data and Data Collection and Refinement Details for $(1)_2\cdot PhMe\cdot {}^1/_2THF$

	Crystal Data
formula	$(C_{50}H_{44}O_4P_2Pt)_2\cdot C_7H_8\cdot {}^1/_2(C_4H_8O)$
fw	2060.06
space group	$P2_1/n$
a, Å	12.750(2)
b, Å	18.503(4)
c, Å	39.648(6)
β, deg	94.69(1)
V, Å^3	9322(5)
Z	4
D_{calcd}, g cm^{-3}	1.47
cryst size, mm	0.38 × 0.38 × 0.58
linear abs coeff, cm^{-1}	31.52
	Data Collection and Refinement
temp, °C	22
diffractometer	Rigaku AFC5S
radiation (λ, Å)	Mo Kα with graphite monochromator (0.710 73)
transm factors	0.77−1.0 (empirical ψ scan method)
2θ limits, deg	4−50
scan speed, deg min^{-1} (in ω)	4 (3 rescans)
scan type	ω
scan range, deg (in ω)	$0.90 + 0.35 \tan \theta$
data collcd	$+h,+k,\pm l$
no. of reflns measd	17 795 (total), 16 980 (unique, $R_{int} = 0.041$)
no. of reflns used ($I > 3\sigma(I)$)	9982
no. of variables	1070
$R(F)$	0.045
$R_w(F)^a$	0.050
error in obsn of unit wt, e	1.56
max peak in final diff map, e Å^{-3}	1.47
min peak in final diff map, e Å^{-3}	−1.40

^{a} $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, with $w = 1/\sigma^2(F_o)$.

There are two Pt complexes in the asymmetric unit. The positions for the two Pt atoms were found via the Patterson method, and the rest of the atoms were obtained by the DIRDIF procedure[13] and by standard Fourier methods. The two Pt complexes are labeled as A and B. The asymmetric unit also contains a toluene molecule (C(151)−C(157)) which was modeled with a rigid group.[14] There appears to be a disordered THF molecule located about an inversion center. One of the atoms of the THF molecule resides on the inversion center, which makes it common to both sites of the molecule. All atoms in the THF molecule are labeled as carbon atoms (C(201)−C(205)) and given occupancy factors of 0.5. Thus the asymmetric unit is composed of two Pt complexes, one toluene molecule, and a half of a THF molecule.

Full-matrix least-squares refinements were done in TEXSAN; the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The data were corrected for absorption using the empirical ψ scan method.[15] One of the ester groups in Pt complex A is disordered over two sites and was modeled in terms of two sets of atoms: C(7A), O(3A), O(4A), C(8A) and C(7AA), O(3AA), O(4AA), C(8AA). The occupancy factor for one of these atoms was refined while the occupancy factors for the other atoms were constrained accordingly. As a result, fragment A has an occupancy factor of 0.56 while fragment

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(12) TEXSAN, Single Crystal Structure Analysis Software, Version 5.0, 1989; Molecular Structure Corp., The Woodlands, TX 77381.

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Table 2. Positional and Equivalent Isotropic Thermal Parameters for (1)$_2$·PhMe·$^1/_2$THF^a

atom	x	y	z	$B_{eq}{}^b$ or B, Å^2	atom	x	y	z	$B_{eq}{}^b$ or B, Å^2
Pt(1A)	0.40685(3)	0.16701(2)	0.09771(1)	3.25(2)	O(2B)	0.6190(7)	0.0098(5)	0.3720(2)	8.0(5)
P(1A)	0.3064(2)	0.1845(1)	0.14199(6)	3.7(1)	O(3B)	0.7056(7)	0.0465(5)	0.2877(2)	7.5(5)
P(2A)	0.2786(2)	0.1694(1)	0.05317(6)	3.7(1)	O(4B)	0.5506(6)	0.0261(5)	0.3066(2)	7.1(5)
O(1A)	0.6665(7)	0.2413(5)	0.0301(2)	7.8(5)	C(1B)	0.7336(7)	0.2056(5)	0.3021(2)	3.5(5)
O(2A)	0.6909(7)	0.3497(4)	0.0532(2)	6.5(5)	C(2B)	0.7082(7)	0.1737(5)	0.3340(2)	3.5(4)
O(3A)	0.561(1)	0.3232(8)	0.1346(4)	6.4(4)*	C(3B)	0.7645(7)	0.2160(6)	0.3611(2)	3.7(5)
O(3AA)	0.775(2)	0.320(1)	0.1163(5)	6.2(5)*	C(4B)	0.6621(7)	0.1069(6)	0.3379(2)	4.1(5)
O(4A)	0.724(1)	0.3431(8)	0.1248(4)	5.9(3)*	C(5B)	0.6362(9)	0.0816(7)	0.3710(3)	5.1(6)
O(4AA)	0.618(2)	0.317(1)	0.1376(6)	5.8(5)*	C(6B)	0.591(1)	−0.0195(8)	0.4032(4)	10(1)
C(1A)	0.5589(7)	0.1617(6)	0.1239(2)	3.9(5)	C(7B)	0.646(1)	0.0565(6)	0.3092(3)	5.4(6)
C(2A)	0.5855(7)	0.1889(6)	0.0913(3)	4.4(5)	C(8B)	0.539(1)	−0.0253(8)	0.2784(3)	9(1)
C(3A)	0.5312(8)	0.1452(6)	0.0658(3)	4.0(5)	C(9B)	0.6969(7)	0.2811(5)	0.2936(2)	3.7(5)
C(4A)	0.6309(8)	0.2590(6)	0.0870(3)	4.5(5)	C(10B)	0.7405(8)	0.3219(6)	0.2693(3)	4.7(5)
C(5A)	0.6639(9)	0.2795(7)	0.0551(3)	5.3(6)	C(11B)	0.699(1)	0.3883(7)	0.2594(3)	6.0(7)
C(6A)	0.733(1)	0.3741(8)	0.0228(4)	9(1)	C(12B)	0.613(1)	0.4155(7)	0.2743(4)	6.8(8)
C(7A)	0.628(2)	0.315(1)	0.1185(6)	4.5(5)*	C(13B)	0.566(1)	0.3750(7)	0.2977(3)	6.3(7)
C(7AA)	0.679(2)	0.300(1)	0.1123(5)	3.2(4)*	C(14B)	0.6088(8)	0.3085(6)	0.3082(3)	4.7(5)
C(8A)	0.734(2)	0.388(1)	0.1539(6)	6.9(5)*	C(15B)	0.9244(7)	0.1881(5)	0.2419(2)	3.8(5)
C(8AA)	0.663(2)	0.364(2)	0.1648(7)	6.1(6)*	C(16B)	0.9497(8)	0.2406(6)	0.2178(2)	4.5(5)
C(9A)	0.5992(8)	0.0868(6)	0.1335(2)	4.1(5)	C(17B)	0.8978(9)	0.2430(6)	0.1860(3)	5.2(6)
C(10A)	0.6886(8)	0.0591(6)	0.1189(3)	4.9(5)	C(18B)	0.820(1)	0.1935(7)	0.1770(3)	5.9(6)
C(11A)	0.7345(9)	−0.0051(7)	0.1305(3)	5.9(7)	C(19B)	0.7952(9)	0.1422(7)	0.1993(3)	5.9(6)
C(12A)	0.695(1)	−0.0430(7)	0.1562(3)	6.1(7)	C(20B)	0.8462(8)	0.1388(5)	0.2314(2)	4.2(5)
C(13A)	0.607(1)	−0.0159(6)	0.1711(3)	6.4(7)	C(21B)	1.0909(7)	0.2486(5)	0.2847(2)	3.6(5)
C(14A)	0.5594(8)	0.0484(6)	0.1600(2)	4.6(5)	C(22B)	1.1940(9)	0.2374(6)	0.2782(3)	5.2(6)
C(15A)	0.3708(8)	0.1803(6)	0.1845(2)	4.1(5)	C(23B)	1.2662(9)	0.2947(7)	0.2803(3)	6.0(7)
C(16A)	0.4487(9)	0.2300(6)	0.1937(3)	5.5(6)	C(24B)	1.235(1)	0.3605(7)	0.2895(3)	6.2(7)
C(17A)	0.5016(9)	0.2290(7)	0.2265(3)	5.9(7)	C(25B)	1.134(1)	0.3735(6)	0.2967(3)	5.6(6)
C(18A)	0.477(1)	0.1780(8)	0.2489(3)	5.9(7)	C(26B)	1.0624(8)	0.3178(6)	0.2943(3)	4.6(6)
C(19A)	0.400(1)	0.1265(7)	0.2408(3)	5.8(6)	C(27B)	1.0461(7)	0.0913(6)	0.2819(3)	4.2(5)
C(20A)	0.3475(8)	0.1279(6)	0.2086(3)	4.9(6)	C(28B)	1.1132(9)	0.0740(6)	0.2572(3)	6.1(7)
C(21A)	0.2038(8)	0.1163(6)	0.1427(2)	4.1(5)	C(29B)	1.156(1)	0.0046(9)	0.2569(5)	9(1)
C(22A)	0.240(1)	0.0459(7)	0.1368(3)	5.9(7)	C(30B)	1.131(1)	−0.0462(8)	0.2802(5)	8(1)
C(23A)	0.167(1)	−0.0119(7)	0.1366(4)	7.8(9)	C(31B)	1.063(1)	−0.0296(7)	0.3041(4)	7.8(8)
C(24A)	0.063(1)	0.002(1)	0.1424(4)	8(1)	C(32B)	1.0194(9)	0.0391(6)	0.3044(3)	5.0(6)
C(25A)	0.032(1)	0.070(1)	0.1488(4)	8(1)	C(33B)	1.1573(7)	0.1893(6)	0.3650(2)	4.0(5)
C(26A)	0.0997(9)	0.1273(7)	0.1486(3)	6.2(7)	C(34B)	1.2059(8)	0.1282(6)	0.3548(3)	4.9(6)
C(27A)	0.2481(8)	0.2749(6)	0.1439(3)	4.4(5)	C(35B)	1.313(1)	0.1280(7)	0.3485(3)	5.9(7)
C(28A)	0.279(1)	0.3277(7)	0.1223(3)	6.0(7)	C(36B)	1.369(1)	0.1904(8)	0.3524(4)	7.0(8)
C(29A)	0.239(2)	0.3969(9)	0.1236(4)	9(1)	C(37B)	1.323(1)	0.2524(7)	0.3621(3)	6.3(7)
C(30A)	0.165(2)	0.412(1)	0.1460(7)	12(1)	C(38B)	1.2167(8)	0.2516(6)	0.3685(3)	5.1(6)
C(31A)	0.140(1)	0.361(1)	0.1684(6)	11(1)	C(39B)	1.0064(8)	0.1047(5)	0.3962(2)	4.4(5)
C(32A)	0.181(1)	0.2921(7)	0.1687(4)	7.8(8)	C(40B)	1.0842(9)	0.0816(7)	0.4200(3)	6.0(6)
C(33A)	0.1391(8)	0.1772(6)	0.0601(2)	4.3(5)	C(41B)	1.072(1)	0.0193(8)	0.4376(4)	8.0(9)
C(34A)	0.0699(9)	0.1184(7)	0.0594(3)	6.1(7)	C(42B)	0.984(1)	−0.0223(8)	0.4317(4)	8.0(9)
C(35A)	−0.035(1)	0.128(1)	0.0659(4)	8(1)	C(43B)	0.906(1)	−0.0005(6)	0.4088(3)	5.9(6)
C(36A)	−0.072(1)	0.191(1)	0.0728(4)	7.6(9)	C(44B)	0.9171(8)	0.0620(6)	0.3906(2)	4.6(5)
C(37A)	−0.009(1)	0.2508(8)	0.0734(3)	7.4(8)	C(45B)	1.0034(7)	0.2614(6)	0.4019(2)	4.1(5)
C(38A)	0.097(1)	0.2443(7)	0.0672(3)	5.9(7)	C(46B)	0.980(1)	0.3292(7)	0.3897(3)	6.8(7)
C(39A)	0.2978(8)	0.2427(5)	0.0237(2)	4.1(5)	C(47B)	0.975(1)	0.3900(7)	0.4102(4)	8.3(8)
C(40A)	0.3837(7)	0.2882(5)	0.0276(2)	4.1(5)	C(48B)	0.991(1)	0.379(1)	0.4441(4)	8(1)
C(41A)	0.398(1)	0.3424(6)	0.0046(3)	5.6(6)	C(49B)	1.015(1)	0.313(1)	0.4580(3)	9(1)
C(42A)	0.328(1)	0.3518(7)	−0.0228(3)	6.4(7)	C(50B)	1.022(1)	0.2545(7)	0.4356(3)	6.5(7)
C(43A)	0.240(1)	0.3090(8)	−0.0273(3)	7.1(8)	C(201)	0.620(2)	0.038(2)	0.5307(7)	7.0(6)*
C(44A)	0.2249(9)	0.2551(7)	−0.0041(3)	5.6(6)	C(202)	0.565(3)	0.046(2)	0.5092(9)	9.0(8)*
C(45A)	0.2855(8)	0.0861(6)	0.0287(3)	4.2(5)	C(203)	0.497(2)	0.066(2)	0.4871(7)	7.9(7)*
C(46A)	0.289(1)	0.0215(7)	0.0462(3)	7.0(8)	C(204)	0.593(3)	−0.037(2)	0.5366(9)	11(1)*
C(47A)	0.291(1)	−0.0440(7)	0.0300(4)	8.1(9)	C(205)	$^1/_2$	0	$^1/_2$	20(1)*
C(48A)	0.291(1)	−0.046(1)	−0.0049(5)	8(1)	C(151)	0.0922(8)	0.1242(8)	0.9215(3)	14.6(3)**
C(49A)	0.292(1)	0.016(1)	−0.0214(4)	10(1)	C(152)	0.071(1)	0.1966(8)	0.9139(3)	14.6(3)**
C(50A)	0.288(1)	0.0813(7)	−0.0055(3)	7.5(8)	C(153)	−0.004(1)	0.2341(5)	0.9307(3)	14.6(3)**
Pt(1B)	0.88736(3)	0.19664(2)	0.328333(9)	2.99(2)	C(154)	−0.0576(7)	0.1991(6)	0.9553(2)	14.6(3)**
P(1B)	0.9876(2)	0.1808(1)	0.28384(6)	3.4(1)	C(155)	−0.037(1)	0.1267(6)	0.9630(3)	14.6(3)**
P(2B)	1.0177(2)	0.1881(1)	0.37222(6)	3.6(1)	C(156)	0.038(1)	0.0892(5)	0.9461(4)	14.6(3)**
O(1B)	0.6297(7)	0.1185(5)	0.3957(2)	7.6(5)	C(157)	−0.140(1)	0.2402(9)	0.9738(4)	14.6(3)**

[a] Estimated standard deviations in the least significant figure are given in parentheses. Atoms O(3A), O(4A), C(7A), and C(8A) have occupancy factors of 0.56. O(3AA), O(4AA), C(7AA), and C(8AA) have occupancy factors of 0.44. C(201), C(202), C(203), C(204) and C(205) have occupancy factors of 0.5. [b] The form of the equivalent isotropic displacement parameter is $B(\text{eq}) = (8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$. Asterisks designate B values for atoms refined isotropically. Double asterisks designate B values for atoms refined as part of a rigid group.

AA is at 0.44. Because of the disorder, the geometry for thisportion of molecule A is not as well defined as it is in molecule B. The disordered ester group, the THF molecule, and the rigid toluene group were all kept isotropic. All of the other non-hydrogen atoms were refined anisotropically. The hydrogen atoms for the Pt complexes were included in the model as fixed contributions in calculated positions with C−H = 0.98 Å and $B_H = 1.2B(\text{eq})$ (attached carbon atom). The three trimethylenemethane hydrogen atoms for each complex were refined isotropically (H(71)−(H(76)). One of these, H(75), acquired a large B value. Its B value was then fixed at 3 Å^2 for subsequent refinements, and only its positional parameters were refined. Methyl hydrogen atoms were idealized to sp^3 geometry based on positions located in difference electron density maps. No hydrogen atoms were added to the toluene and THF molecules.

Scattering factors for neutral atoms, along with terms for anomalous dispersion, were used.[16] Several reflections with uneven backgrounds were removed from the data set: $(0,3,\overline{20})$, $(2,1,\overline{25})$, $(2,1,15)$, $(1,1,\overline{12})$, $(0,3,\overline{22})$, $(0,3,22)$, $(3,2,17)$, and $(4,4,12)$.

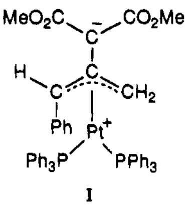
A summary of the crystal data and the details of the intensity data collection and refinement are provided in Table 1. Final positional and equivalent isotropic thermal parameters are given in Table 2. Lists of anisotropic thermal parameters and bond distances and angles are available as supplementary material.[17]

Results and Discussion

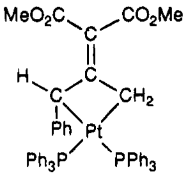
Synthesis of 1. Reaction of the η^3-propargyl/allenyl complex [(PPh$_3$)$_2$Pt(η^3-CH$_2$CCPh)]O$_3$SCF$_3$ with 1 equiv of Na[CH(CO$_2$Me)$_2$] in CH$_2$Cl$_2$ at room temperature affords the trimethylenemethane product **1** in 83% isolated yield (cf. eq 2). Complex **1** can also be obtained, more conveniently, by reaction of (PPh$_3$)$_2$Pt(C$_2$H$_4$) with PhC≡CCH$_2$OTs (Ts = *p*-MeC$_6$H$_4$SO$_2$) and Na[CH(CO$_2$Me)$_2$] in CH$_2$Cl$_2$; however, conditions for this "one-pot" synthesis have yet to be optimized.

The formation of **1** by reaction of [(PPh$_3$)$_2$Pt(η^3-CH$_2$CCPh)]$^+$ with CH(CO$_2$Me)$_2^-$ would appear to involve addition of H—C(CO$_2$Me)$_2^-$ to the orthogonal, uncoordinated C═C π bond of $CH_2\overset{-}{\cdots}C\overset{=}{\cdots}CPh$, with the C(CO$_2$Me)$_2$ group adding to the central carbon atom and hydrogen adding to the terminal carbon atom *C*Ph. In this respect, the transformation depicted in eq 2 seems similar to that in eq 1 for NuH being ROH, RNH$_2$, R$_2$NH, and RSH. The mechanism of these unusual addition reactions to η^3-CH$_2$CCR is presently under investigation.

Characterization of 1. Complex **1** was obtained as a yellow-orange solid that is stable to air. Both ^{1}H and ^{13}C{^{1}H} NMR spectra at ambient temperature support η^3 bonding of the organic ligand to platinum. In the former spectrum, separate allylic proton signals are observed at δ 5.38, 4.00, and 2.60, the last one with a rather substantial geminal coupling constant of 4.2 Hz for the CH$_2$ group. This value of $^2J_{HH}$ suggests[18] a contribution from the platinacyclic resonance form **II** to the overall bonding description of **1**. Only one proton signal occurs for the CO$_2$Me groups, presumably owing to rapid rotation about the C═C bond (cf. **II**).[4] The ^{13}C{^{1}H} NMR spectrum shows two resonances at δ 70.7 and 46.6 with large J_{PtC} coupling constants (227 and 159 Hz, respectively), assigned to the *C*HPh and CH$_2$ carbon atoms, and another resonance at δ 149.2 with a smaller J_{PtC} coupling constant (91 Hz), assigned to the central carbon atom. These ^{13}C chemical shifts and coupling constants suggest a major contribution to the bonding of the η^3-allyl resonance form **I**.[19] An additional signal at δ 88.4 with no observable J_{PtC} is attributed to the uncoordinated *C*(CO$_2$Me)$_2$ carbon atom, in agreement with the proposed η^3-trimethylenemethane structure. The two CO$_2$Me groups appear equivalent, as they do in the ^{1}H NMR spectrum.



I



II

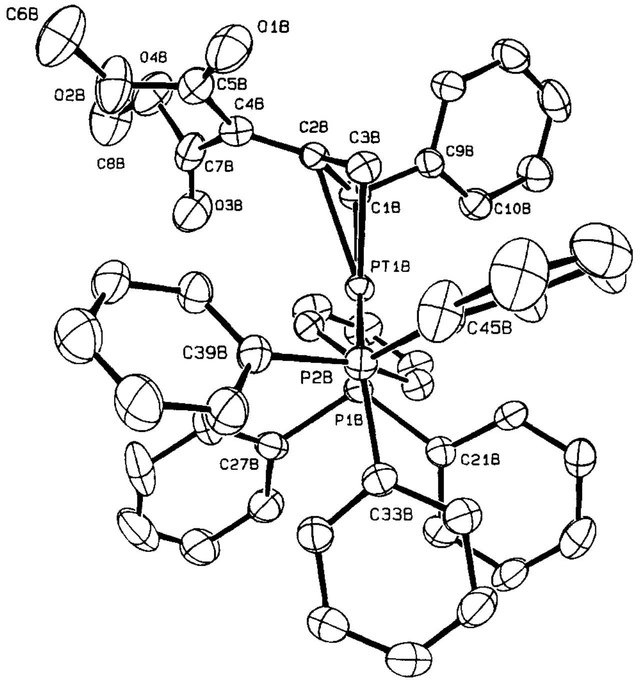


Figure 1. ORTEP drawing of **1** showing the atom-numbering scheme. The non-hydrogen atoms are drawn at the 30% probability level, and the hydrogen atoms are omitted.

Although the foregoing spectra implicate a platinum–η^3-trimethylenemethane mode of bonding, an X-ray diffraction study of **1** (actually, of (**1**)$_2$·PhMe·1/2THF) was undertaken to unequivocally confirm the structure and to obtain important metrical data. The structures of several transition-metal trimethylenemethane complexes have been established by X-ray diffraction techniques.[2a] However, until we reported the synthesis of **1**,[3] no group 10 L$_n$*M*(trimethylenemethane) complexes had been isolated and characterized.

Crystals of (**1**)$_2$·PhMe·1/2THF contain two crystallographically independent molecules A and B of **1** that differ in the orientation of the CO$_2$Me groups. An ORTEP drawing of molecule B is shown in Figure 1. Selected bond distances and angles are given in Table 3.

Molecules of **1** contain a trimethylenemethane ligand, CH$_2$C(C(CO$_2$Me)$_2$)CHPh, which is bonded to platinum in an η^3 rather than an η^4 fashion, as proposed by Trost[20] and Albright.[21] The phenyl substituent on C(1)

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(16) Scattering factors for the non-hydrogen atoms, including terms for anomalous dispersion, are from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 71, 148. The scattering factor for the hydrogen atom is from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(17) See the paragraph at the end of the paper regarding supplementary material.

(18) For example, for metallacyclobutene complexes see: Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597.

(19) (a) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257. (b) Gregg, M. R.; Powell, J.; Sawyer, J. F. *J. Organomet. Chem.* **1988**, *352*, 357 and references therein.

(20) (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1980**, *102*, 6359. (b) Gordon, D. J.; Fenske, R. F.; Nanninga, T. M.; Trost, B. M. *J. Am. Chem. Soc.* **1981**, *103*, 5974.

Table 3. Selected Bond Distances (Å) and Angles (deg) for (1)$_2$·PhMe·$^1/_2$THF

	Bond Distances		
Pt(1A)—P(1A)	2.279(3)	Pt(1B)—P(1B)	2.280(3)
Pt(1A)—P(2A)	2.307(2)	Pt(1B)—P(2B)	2.311(2)
Pt(1A)—C(1A)	2.126(9)	Pt(1B)—C(1B)	2.149(9)
Pt(1A)—C(2A)	2.348(10)	Pt(1B)—C(2B)	2.352(9)
Pt(1A)—C(3A)	2.146(11)	Pt(1B)—C(3B)	2.146(10)
C(1A)—C(2A)	1.45(1)	C(1B)—C(2B)	1.46(1)
C(1A)—C(9A)	1.52(1)	C(1B)—C(9B)	1.50(1)
C(2A)—C(3A)	1.43(1)	C(2B)—C(3B)	1.47(1)
C(2A)—C(4A)	1.44(2)	C(2B)—C(4B)	1.38(1)
C(4A)—C(5A)	1.42(2)	C(4B)—C(5B)	1.46(2)
C(4A)—C(7A)	1.62(2)	C(4B)—C(7B)	1.47(2)
C(4A)—C(7AA)	1.37(2)	O(1B)—C(5B)	1.20(1)
O(1A)—C(5A)	1.22(2)	O(3B)—C(7B)	1.21(2)
O(3A)—C(7A)	1.13(3)		
O(3AA)—C(7AA)	1.27(3)		
	Bond Angles		
P(1A)—Pt(1A)—P(2A)	100.31(9)	P(1B)—Pt(1B)—P(2B)	99.19(9)
P(1A)—Pt(1A)—C(1A)	100.2(3)	P(1B)—Pt(1B)—C(1B)	100.5(3)
P(1A)—Pt(1A)—C(2A)	132.1(3)	P(1B)—Pt(1B)—C(2B)	131.4(2)
P(1A)—Pt(1A)—C(3A)	165.8(3)	P(1B)—Pt(1B)—C(3B)	166.7(2)
P(2A)—Pt(1A)—C(1A)	159.4(3)	P(2B)—Pt(1B)—C(1B)	160.2(3)
P(2A)—Pt(1A)—C(2A)	123.2(3)	P(2B)—Pt(1B)—C(2B)	124.0(2)
P(2A)—Pt(1A)—C(3A)	93.7(3)	P(2B)—Pt(1B)—C(3B)	94.1(2)
C(1A)—Pt(1A)—C(2A)	37.5(4)	C(1B)—Pt(1B)—C(2B)	37.4(3)
C(1A)—Pt(1A)—C(3A)	65.9(4)	C(1B)—Pt(1B)—C(3B)	66.3(3)
C(2A)—Pt(1A)—C(3A)	36.7(4)	C(2B)—Pt(1B)—C(3B)	37.8(3)
Pt(1A)—C(1A)—C(2A)	79.6(5)	Pt(1B)—C(1B)—C(2B)	78.9(5)
Pt(1A)—C(1A)—C(9A)	116.3(7)	Pt(1B)—C(1B)—C(9B)	115.8(6)
C(2A)—C(1A)—C(9A)	116.1(9)	C(2B)—C(1B)—C(9B)	119.0(8)
Pt(1A)—C(2A)—C(1A)	62.9(5)	Pt(1B)—C(2B)—C(1B)	63.7(5)
Pt(1A)—C(2A)—C(3A)	63.9(6)	Pt(1B)—C(2B)—C(3B)	63.5(5)
Pt(1A)—C(2A)—C(4A)	124.9(7)	Pt(1B)—C(2B)—C(4B)	126.7(7)
C(1A)—C(2A)—C(3A)	107.4(9)	C(1B)—C(2B)—C(3B)	106.7(8)
C(1A)—C(2A)—C(4A)	123.0(9)	C(1B)—C(2B)—C(4B)	125.9(9)
C(3A)—C(2A)—C(4A)	127.0(10)	C(3B)—C(2B)—C(4B)	125.7(9)
Pt(1A)—C(3A)—C(2A)	79.3(6)	Pt(1B)—C(3B)—C(2B)	78.8(5)
C(2A)—C(4A)—C(5A)	120(1)	C(2B)—C(4B)—C(5B)	121(1)
C(2A)—C(4A)—C(7A)	117(1)	C(2B)—C(4B)—C(7B)	121(1)
C(2A)—C(4A)—C(7AA)	125(1)	C(5B)—C(4B)—C(7B)	118(1)
C(5A)—C(4A)—C(7A)	123(1)	O(1B)—C(5B)—O(2B)	121(1)
C(5A)—C(4A)—C(7AA)	111(1)	O(1B)—C(5B)—C(4B)	126(1)
O(1A)—C(5A)—O(2A)	119(1)	O(2B)—C(5B)—C(4B)	113(1)
O(1A)—C(5A)—C(4A)	127(1)	O(3B)—C(7B)—O(4B)	120(1)
O(2A)—C(5A)—C(4A)	114(1)	O(3B)—C(7B)—C(4B)	126(1)
O(3A)—C(7A)—O(4A)	125(2)	O(4B)—C(7B)—C(4B)	113(1)
O(3AA)—C(7AA)—O(4AA)	117(2)		
O(3A)—C(7A)—C(4A)	126(2)		
O(3AA)—C(7AA)—C(4A)	128(2)		
O(4A)—C(7A)—C(4A)	109(2)		
O(4AA)—C(7AA)—C(4A)	115(2)		

is oriented anti to the C(CO$_2$Me)$_2$ group on C(2). The average value of the C(1)—C(2)—C(3) angle of the η^3-bonded C$_3$ fragment in **1** of 107.0(9)° may be compared with that of ca. 120° in metal η^3-allyl complexes[22] and of 97.5(5)° in the platinacyclobutane complex (PEt$_3$)$_2$Pt(η^2-CH$_2$CMe$_2$CH$_2$).[23] The dihedral (fold) angle between the planes C(1)—Pt—C(3) and C(1)—C(2)—C(3) of 59.9° (average) underscores the importance of the η^3-allyl resonance structure **I**. This value is substantially larger than that observed for platinacyclobutane complexes, 0–30°,[23–25] and only somewhat smaller than that reported for η^3-allyl complexes of platinum(II) and palladium(II) without a central carbon–heteroatom bond, 61–72°.[22,26] The related platinum η^3-oxoallyl complexes (PPh$_3$)$_2$Pt(η^3-CH$_2$C(O)CH$_2$), (PPh$_3$)$_2$Pt(η^3-CH(COMe)C)(O)CH(COMe)), and (PPh$_3$)$_2$Pt(η^3-CH(CO$_2$Me)C(O)CH(CO$_2$Me)) and the η^3-aminoallyl complexes [(PPh$_3$)$_2$Pt(η^3-CH$_2$C(NMe$_2$)CH$_2$]BF$_4$ and [(PPh$_3$)$_2$Pt(η^3-CH$_2$C(NH*i*-Pr)CH$_2$]Br show the fold angles of 51.0,[27] 48.0(4),[28] 50.4(4),[29] 54(2),[30] and 57(2)°,[30] respectively, all smaller than that for **1**.

Electron delocalization over the η^3 ligand of **1** is evidenced by the values of the C—C bond distances, which average 1.45(1) Å. These distances are longer than the typical C—C distances (1.40 Å) in normal L$_2$M(η^3-allyl) (M = Pt, Pd) complexes[22,26] but shorter than those in platinacyclobutane complexes, which correspond to C—C single bonds.[23,24] Moreover, the average Pt—C(terminal) bond distances in **1** (Pt—C(1) = 2.138(9) Å, Pt—C(3) = 2.146(10) Å) are essentially comparable to those in the η^3-allyl and η^3-oxoallyl complexes [(PCy$_3$)$_2$Pt(η^3-CH$_2$CHCH$_2$)]PF$_6$ (2.17(5) Å average)[31] and (PPh$_3$)$_2$Pt(η^3-CH$_2$C(O)CH$_2$) (2.132(12) Å average),[27] respectively, but are longer than those in the platinacyclobutane complex (PEt$_3$)$_2$Pt(η^2-CH$_2$CMe$_2$CH$_2$) (2.083(6) Å average).[23] The Pt—C(central) bond length (2.350(10) Å average) is ca. 0.21 Å greater than the average Pt—C(terminal) bond length in **1**. It may be compared with the corresponding bond distance in the aforementioned platinum η^3-allyl (2.24(2) Å)[31] and η^3-oxoallyl (2.422(12) Å)[27] complexes and contrasted with the nonbonding transannular Pt—C separation in the platinacycle (PEt$_3$)$_2$Pt(η^2-CH$_2$CMe$_2$CH$_2$) (2.76 Å).[32]

The coordination environment of C(1), C(3), P(1), and P(2) around the platinum center in **1** is very close to being square planar, with the average dihedral angle between the C(1)—Pt—C(3) and P(1)—Pt—P(2) planes being 3.2°. Such a local coordination at the metal is favored on theoretical grounds for 16-electron L$_2$M(η^3-allyl) complexes.[33] All three allylic carbon atoms show varied degrees of pyramidalization. Thus, the sum of the bond angles average 347° around C(1) and C(3) and 357.8° around C(2). The carbon atom C(4), positioned 0.31 Å (average) away from the C(1)—C(2)—C(3) plane, is coplanar with C(2), C(5), and C(7). As a result of the slight pyramidalization at C(2), and also owing to a nonzero torsion angle about the C(2)—C(4) bond, the angle between the planes C(1)—C(2)—C(3) and C(5)—C(4)—C(7) averages 18.2°.

Reactions of 1. Transition-metal trimethylenemethane complexes generally undergo addition of electrophilic reagents to the organic ligand.[2a] Thus, for example, (CO)$_3$Fe(η^4-CH$_2$C(CH$_2$)CH$_2$) reacts with HCl to afford Cl(CO)$_3$Fe(η^3-CH$_2$C(Me)CH$_2$).[34] Protonation experiments have also been conducted in support of the involvement of an η^3-trimethylenemethane complex in

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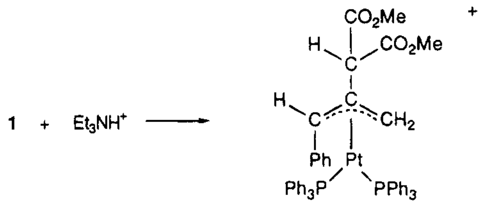
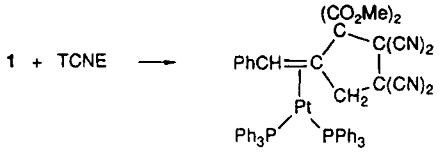
the Pd(0)-catalyzed cycloaddition of a trimethylenemethane fragment to electron-deficient olefins.[20a]

We find that **1** readily reacts with $[Et_3NH]BPh_4$ by exclusive protonation at the $C(CO_2Me)_2$ carbon atom to yield the η^3-allyl complex **2** (eq 3). The structure of the product is assigned from NMR spectroscopic evidence. In addition to the three allylic ^1H NMR signals at δ 5.59, 3.80, and 3.10, a resonance is observed at δ 4.11 with J_{PtH} = 15 Hz for the $CH(CO_2Me)_2$ hydrogen. The appearance of two proton signals for CO_2Me at δ 3.82 and 3.74 accords with the asymmetry of the cationic complex. Two signals are also noted for CO_2Me in the $^{13}C\{^1H\}$ NMR spectrum, which features resonances typical of metal η^3-allyl complexes.[19]



2 (3)

The trimethylenemethane fragment derived from bifunctional conjunctive reagents such as $Me_3SiCH_2C(CH_2)CH_2OAc$ has been shown to undergo chemoselective [3 + 2] cycloaddition to electron-deficient olefins in the presence of a palladium(0) catalyst.[2] To ascertain whether a stable metal η^3-trimethylenemethane complex also participates in [3 + 2] cycloaddition reactions, we checked the behavior of **1** toward a couple of olefins.[35] We find that whereas reaction of **1** with diethyl fumarate in benzene proceeds very slowly at ambient temperature, reaction of **1** with the more electrophilic TCNE goes to completion within 1 h under similar conditions (eq 4). TCNE is known to participate in a large number of [3 + 2] cycloaddition reactions,[36] even though electron transfer processes have precluded its use in Pd-catalyzed trimethylenemethane cycloaddition reactions.[8a]



3 (4)

The organometallic product **3** has been characterized as a platinum(0) olefin complex, with the olefin being derived by [3 + 2] cycloaddition of TCNE to the trimethylenemethane ligand of **1**. The ^1H NMR spectrum shows three signals, in addition to those of the Ph rings and the inequivalent CO_2Me groups. Two of these signals, at δ 3.04 and 2.16, are assigned to the inequivalent protons of the ring CH_2 group on the basis of their position and a large value of the geminal H–H coupling constant.[37] The third signal, at δ 6.19, is attributed to the $PhCH{=}C$ proton of the coordinated double bond. These assignments were aided by selective decoupling experiments. In the $^{13}C\{^1H\}$ NMR spectrum, separate signals are observed for each of the two inequivalent CO_2Me, CO_2Me, and $C(CN)_2$ carbon atoms, and three signals for the four inequivalent CN carbon atoms (relative intensities 1:1:2), as expected for structure **3**. Elemental analysis supports the chemical composition of **3**.

We are exploring synthesis of other metal trimethylenemethane complexes and heteroatom analogues, as well as their reactions with unsaturated compounds.

Acknowledgment. V.P. and P.W.B. thank the Lubrizol Co. and the Procter and Gamble Co., respectively, for graduate fellowships.

Supplementary Material Available: Tables of anisotropic thermal parameters and bond distances and angles for complex **1** (15 pages). Ordering information is given on any current masthead page.

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(35) A more comprehensive study of such reactions will be carried out on a series of similar platinum trimethylenemethane complexes and various unsaturated compounds.

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