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Tuning of the Electronic and Optical Properties of Manganese(I) Sesquifulvalene Complexes

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Template syntheses of sesquifulvalenes (2,4,6-cycloheptatrien-1-ylidene)cyclopentadiene (**1**) and [(2,4,6-cycloheptatrien-1-ylidene)ethenylidene]cyclopentadiene (**2**) lead to air-stable complexes [(**1**)Mn(CO)$_2$L]BF$_4$ (**4**) and [(**2**)Mn(CO)$_2$L]BF$_4$ (**8**) (**a**, L = CO; **b**, L = P(OMe)$_3$; **c**, L = PPh$_3$). The different σ-donor/π-acceptor abilities of the ligands L allow a tuning of the electronic and optical properties of complexes **4** and **8**, which are particularly studied by UV/vis spectroscopy. The first molecular hyperpolarizabilities β of complexes **4** and **8** have been determined in dichloromethane and acetonitrile solutions by hyper Raleigh scattering. The X-ray crystal structures of **4b**, **8b**, and of the alkenylcyclopentadienyl complex [4,5η-(2,4,6-cycloheptatrien-1-yl)-η^5-cyclopentadienyl]dicarbonylmanganese(I) (**5**) are reported.

Introduction

In recent years, the development and synthesis of new materials with large optical nonlinearities have become an important area of research.[1] With a few exceptions[2] the majority of organic compounds exhibiting large SHG (second harmonic generation) efficiencies are polarizable dipolar molecules with a π-conjugated electron-donor-acceptor arrangement. These requirements are fulfilled by sesquifulvalene (**1**), and substantial first molecular hyperpolarizabilities β have been predicted for sesquifulvalene derivatives based on theoretical calculations.[3] As the instability[4] of **1** does prevent applications in optical device technology, no experimental studies of the nonlinear optical properties of **1** or related organic derivatives thereof had been undertaken. In contrast, complexation of **1** by transition metal fragments leads to stable organometallic compounds,[5−7] which are currently receiving considerable attention in the field of nonlinear optics.[8] We had therefore initiated a program to synthesize stable organometallic complexes of the sesquifulvalene derivatives (**1**) and (**2**) (Figure 1) as potential candidates for nonlinear optical applications and reported on the template syntheses of **1** and **2** at the Mn(CO)$_3$ metal fragment giving complexes **4a** and **8a**.[7] Independently of our approach, Heck et al. have recently published heterobimetallic iron/chromium sesquifulvalene derivatives. These complexes exhibit first molecular hyperpolarizabilities that are among the highest values ever measured for organometallic complexes.[6]

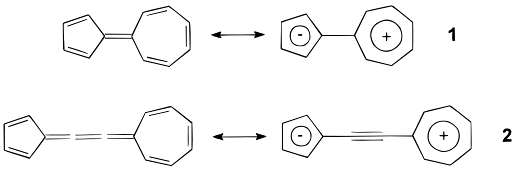

Figure 1. Canonical presentations for sesquifulvalene derivatives.

The two-level model is a simple tool to describe the β response of a π-conjugated donor/acceptor molecule in terms of its electronic and spectroscopic properties.[9]

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(1) (a) Williams, D. J. *Angew. Chem.* **1984**, *96*, 637; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. (b) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando, Fl, 1987. (c) Burland, D. M. *Chem. Rev.* **1994**, *94*, 1. (d) Marks, T. J.; Ratner, M. A. *Angew. Chem.* **1995**, *107*, 167; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155.

(2) (a) Lambert, C.; Stadler, S.; Bourhill, G.; Bräuchle, C. *Angew. Chem.* **1996**, *108*, 710; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 644. (b) Bahl, A.; Grahn, W.; Stadler, S.; Feiner, F.; Bourhill, G.; Bräuchle, C.; Reisner A.; Jones, P. G. *Angew. Chem.* **1995**, *107*, 1587; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1485. (c) Dhenaut, C.; Ledoux, I.; Samuel, I. D. W.; Zyss, J.; Bourgault, M.; Le Bozec, H. *Nature* **1995**, *374*, 339. (d) Ashwell, G. J.; Jefferies, G.; Hamilton, D. G.; Lynch, D. E.; Roberts, M. P. S.; Bahra, G. S.; Brown C. R. *Nature* **1995**, *375*, 385.

(3) Morley, J. O. *J. Am. Chem. Soc.* **1988**, *110*, 7660.

(4) (a) Bingmann, H.; Beck, A.; Fritz, H.; Prinzbach, H. *Chem. Ber.* **1981**, *114*, 1679. (b) Schenk, W. K.; Kyburz, R.; Neuenschwander, M. *Helv. Chim. Acta* **1975**, *58*, 1099.

(5) (a) Cais, M.; Eisenstadt, A. *J. Am. Chem. Soc.* **1967**, *89*, 5468. (b) Brownstein, S. K.; Gabe, E. J.; Hynes, R. C. *Can. J. Chem.* **1992**, *70*, 1011.

(6) Behrens, U.; Brussard, H.; Hagenau, U.; Heck, J.; Hendrickx, E.; Körnich, J.; van der Linden, J. G. M.; Persoons, A.; Spek, A. L.; Veldman, N.; Voss, B.; Wong, H. *Chem. Eur. J.* **1996**, *2*, 98.

(7) Tamm, M.; Grzegorzewski, A.; Brüdgam, I. *J. Organomet. Chem.* **1996**, *519*, 217.

(8) Long, N. J. *Angew. Chem.* **1995**, *107*, 37; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 6.

(9) (a) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664. (b) Hendrickx, E.; Clays, K.; Persoons, A.; Dehu, C.; Bredas, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 3547.

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$$\beta_o = \frac{3\,\Delta\mu_{eg}\,M_{eg}^2}{(h\omega_{eg})^2} \qquad (1)$$

Figure 2.

Equation 1 (Figure 2) shows that the static first molecular hyperpolarizability β_o depends on the dipole moment difference $\Delta\mu_{eg}$, the electronic transition moment M_{eg} and the energy of transition $h\omega_{eg}$, respectively, between the ground state g and excited state e of an intramolecular charge transfer excitation. This correlation expressed by eq 1 clearly shows one major obstacle to designing effective push−pull NLO chromophores ("nonlinearity-transparency trade-off"):[10] on the one hand, it is desirable to lower the energy of the CT transition in order to increase β_o, which does result in compounds with long-wave absorptions;[11] on the other hand, the use of a second-order NLO material for laser frequency doubling (second harmonic generation) requires the compound to be transparent for the laser wavelength λ as well as for $\lambda/2$.[2a,b,10] For instance, in the technically significant doubling of diode laser frequencies[12] absorptions around 800 nm (λ) and 400 nm ($\lambda/2$) should be avoided. Furthermore, the method of choice for the determination of β of an ionic compound in solution is the recently developped hyper Raleigh scattering technique.[13] Usually, this experiment is performed with a Nd:YAG laser (λ = 1064 nm) and the frequency-doubled scattered light ($\lambda/2$ = 532 nm) is measured. We had therefore assumed that it might be difficult to measure the intensity of the scattered light in the case of the manganese(I) sesquifulvalene complexes **4a** and **8a**, which are red to purple in color and exhibit strong absorptions around 500 nm in their UV/vis spectra.[7]

However, these complexes offer the possibility of tuning their electronic and spectroscopic properties by carbonyl substitution reactions allowing, in principle, the adaptation of this system to a given laser, and in this contribution we wish to report on the syntheses of phosphite (**4b**, **8b**) and phosphine complexes (**4c**, **8c**) derived from **4a** and **8a** along with the first molecular hyperpolarizabilities of complexes **4** and **8**.

Results and Discussion

Synthesis and Characterization of 5. A widely used method for the preparation of $CpMn(CO)_2L$ complexes from $CpMn(CO)_3$ is the photochemical introduction of a labile alkene ligand, e.g. *cis*-cyclooctene, which is then easily substituted by other ligands such as isocyanides or phosphines.[14] A similar route is employed by irridation of complex $(C_7H_7\text{-}\eta^5\text{-}C_5H_4)Mn(CO)_3$ (**3a**), which contains an uncoordinated cycloheptatrienyl unit and does therefore have the possibility of chelate formation (Scheme 1). If the reaction (in cyclohexane) is followed by IR spectroscopy, the CO absorptions of the starting material **3a** at 2024 (A_1) and 1942 cm^{-1} (E) disappear, whereas two new absorptions are observed at 1968 and 1913 cm^{-1}, which can be assigned to the symmetric (A_1) and asymmetric (B_1) stretching modes expected for the alkenylcyclopentadienyl complex **5**. After sublimation **5** is obtained in 61% yield. The ^{1}H and ^{13}C NMR spectra indicate that the 2,4,6-cycloheptatrien-1-yl unit is η^2-coordinated via the 4,5-carbon atoms as these resonances are significantly shifted to higher field upon binding to the metal center. This assumption is confirmed by the X-ray structure analysis (Figure 3).

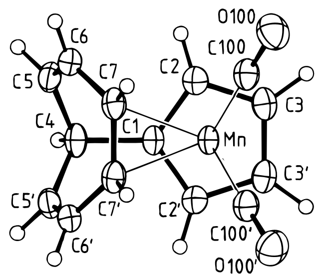
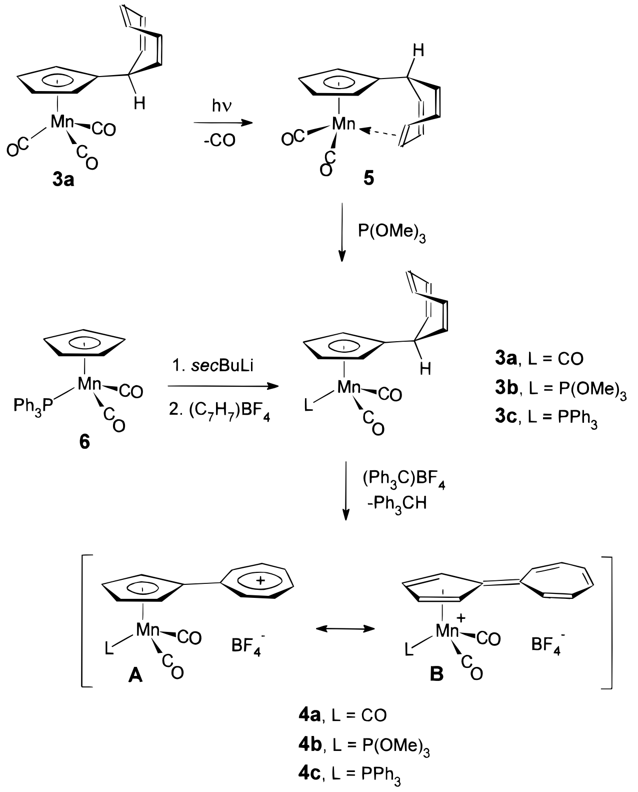


Figure 3. ORTEP drawing of **5**: projection on the cyclopentadienyl plane. Note that the molecule is placed on a crystallographic mirror plane bisecting through C1, C4, and Mn.

Scheme 1



All metal−carbon bond lengths and angles (Table 1) fall in the range observed for other complexes of the type $CpMn(CO)_2(\eta^2\text{-alkene})$.[15] The cycloheptatrienyl unit in **5** adopts a boat conformation and is coordinated without any strain when compared to the structures of cycloheptatriene[16] or substituted cycloheptatriene rings.[17] This perfect fit results in an extraordinary stability of

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(10) Ledoux, I.; Zyss, J.; Jutand, A.; Amatore, C. *Chem. Phys.* **1991**, *150*, 117.

(11) Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* **1991**, *252*, 103

(12) Staring, E. G. J. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 492.

(13) (a) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980. (b) Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1992**, *63*, 3285.

(14) Lentz, D.; Kroll, J.; Langner, C. *Chem. Ber.* **1987**, *120*, 303 and references cited therein.

(15) Selected examples: (a) Vella, P. A.; Beno, M.; Schultz, A. J.; Williams, J. M. *J. Organomet. Chem.* **1981**, *205*, 71. (b) Huttner, G.; Bejenke, V.; Müller, H.-D. *Cryst. Struct. Commun.* **1976**, *5*, 437. (c) Benson, I. B.; Knox, S. A. R.; Stansfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 51.

(16) Traetteberg, M. *J. Am. Chem. Soc.* **1964**, *86*, 4265.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 5

Mn1−C100	1.783(3)	C2−C3	1.422(5)
Mn1−C1	2.109(4)	C3−C3¢	1.399(7)
Mn1−C2	2.133(3)	C1−C4	1.524(5)
Mn1−C3	2.147(3)	C4−C5	1.507(4)
Mn1−C7	2.220(3)	C5−C6	1.322(5)
C100−O100	1.150(4)	C6−C7	1.450(5)
C1−C2	1.419(4)	C7−C7¢	1.409(7)

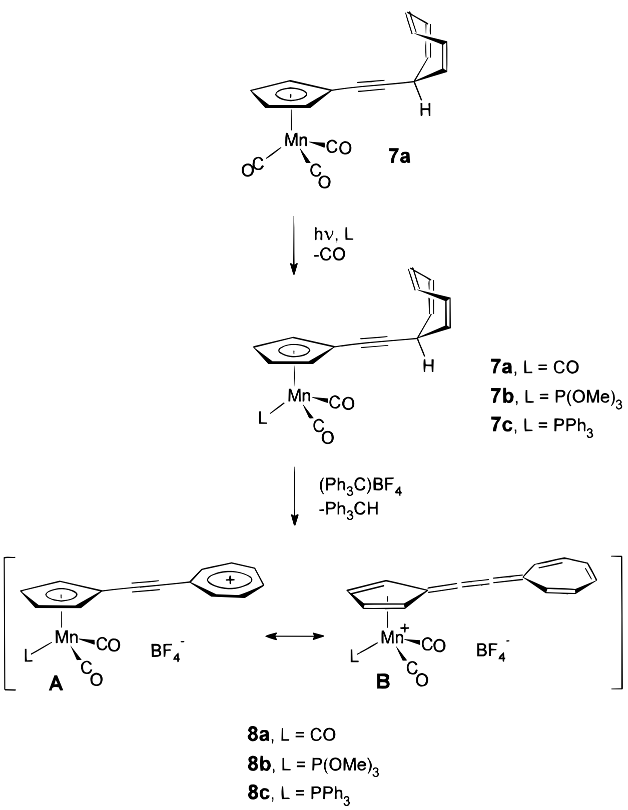
C100−Mn1−C100¢	90.5(2)	C5−C4−C1	110.0(2)
Mn1−C6−C7	115.6(2)	C6−C5−C4	121.5(3)
Mn1−O100−C100	177.4(3)	C5−C6−C7	125.7(3)

5, and replacement of the intramolecular alkene moiety by other ligands only occurs under rather extreme conditions (see below). We are currently investigating the potential of this η^2-C_7H_7−η^5-C_5H_4-system in the synthesis of new alkenylcyclopentadienyl complexes,[18] as these donor-functionalized cyclopentadienyls belong to the growing class of so-called hemilabile ligands, which have received considerable interest in recent years.[19,20]

Syntheses of Sesquifulvalene Complexes. As mentioned above, the introduction of a ligand by an alkene substitution reaction in **5** proves to be comparatively difficult. Whereas CpMn(CO)$_2$(η^2-*cis*-cyclooctene) reacts readily with phosphines and isocyanides,[14] no reaction is observed if **5** is treated with triphenylphosphine or trimethyl phosphite in different solvents at room temperature or under reflux conditions. However, although stirring of **5** in neat trimethyl phosphite does not give any product after 24 h, refluxing (120 °C) this mixture for 60 min results in the almost quantitative formation of **3b**. In contrast, for the synthesis of **3c** a route similar to that reported for **3a** has to be employed (Scheme 1).[7,21] Lithiation of CpMn(CO)$_2$PPh$_3$[22] and consecutive reaction with cycloheptatrienylium tetrafluoroborate, (C_7H_7)BF$_4$, yields **3c**. Hydride abstraction from complexes **3** is best achieved with triphenylcarbenium tetrafluoroborate, (Ph$_3$C)BF$_4$, and the cationic sesquifulvalene complexes **4** are formed almost instantly in CH_2Cl_2 solution. The complexes [(**1**)Mn(CO)$_2$L]BF$_4$ (**4**) are red-purple (**4a**), greenish-blue (**4b**), and blue (**4c**) crystalline compounds.

For the syntheses of the higher "ethynylogues" **8b**,**c** (Scheme 2) the introduction of P(OMe)$_3$ or PPh$_3$ is best achieved by irridation of **7a**[7] in cyclohexane solution with the respective ligand. Here, intramolecular coordination of the cycloheptatrienyl unit as observed by conversion of **3a** into **5** is not possible due to the separation of the five- and seven-membered rings by an acetylenic C_2 bridge. Formation of stable intermolecular alkene complexes is prevented because of the presence of more Lewis basic ligands such as phosphites and phosphines.[14] Complexes [(**2**)Mn(CO$_2$)L]BF$_4$ (**8**) are obtained after hydride abstraction as red (**8a**), greenish-blue (**8b**), and blue (**8c**) crystals.

Scheme 2



Structural Characterization of Sesquifulvalene Complexes 4b and 8b. The molecular structures of the cations in **4b** (top) and **8b** (bottom) are depicted in Figure 4.

The Cp rings are almost coplanar with the seven-membered rings (dihedral angles of 2.4(4)° in **4b** and 3.1(5)° in **8b**). The inter-ring bond distance in **4b** (d(C1−C6) = 1.467(8) Å) is only slightly shorter than expected for a C(sp^2)−C(sp^2) single bond, and in **8b**, the C(sp)−C(sp) bond length (d(C13−C14) = 1.200(14) Å) indicates a triple bond (Table 2).[23] Furthermore, the C_5 and C_7 intra-ring bond lengths do not alternate significantly. These observations indicate that the solid-state structures of **4b** and **8b** are best described as cymatrenyltropylium salts by the canonical forms **A** as shown in Scheme 1 for **4b** and Scheme 2 for **8b**. Comparison of the molecular structures of **4a**[7] and **4b** reveals little sensitivity of the intra-ring C−C bond distances upon the introduction of one phosphite ligand, although the electronic and spectroscopic properties of **4a**,**b** differ significantly (see below).

Spectroscopic Properties of Sesquifulvalene Derivatives. The relative σ-donor/π-acceptor properties

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(17) (a) Bauer, W.; Daub, J.; Maas, G.; Michna, M.; Rapp, K. M.; Stezowski, J. J. *Chem. Ber.* **1982**, *115*, 99. (b) Herberhold, M.; Bauer, K.; Milius, W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 2108.

(18) (a) Okuda, J.; Zimmermann, K. H. *Chem. Ber.* **1989**, *122*, 1645. (b) Okuda, J.; Zimmermann, K. H. *Chem. Ber.* **1990**, *123*, 1641. (c) Okuda, J.; Zimmermann, K. H.; Herdtweck, E. *Angew. Chem.* **1991**, *103*, 446; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 430. (d) Zimmermann, K. H.; Pilato, R. S.; Horvath, I. T.; Okuda, J. *Organometallics* **1992**, *11*, 3935. (e) Lehmkuhl, H.; Näser, J.; Mehler, G.; Keil, T.; Danowski, F.; Benn, R.; Mynott, R.; Schroth, G.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1991**, *124*, 441. (f) Alt, H. G.; Han, J. S.; Rogers, R. D. *J. Organomet. Chem.* **1993**, *445*, 115. (g) Alt, H. G.; Han, J. S.; Thewalt, U. *J. Organomet. Chem.* **1993**, *456*, 89. (h) Ma, Y; Bergman, R. G. *Organometallics* **1994**, *13*, 2548.

(19) For recent reviews, see: (a) Okuda, J. *Comments Inorg. Chem.* **1994**, *16*, 185. (b) Jutzi, P.; Dahlhaus, J. *Coord. Chem. Rev.* **1994**, *137*, 179. (c) Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175.

(20) For recent publications, see: (a) Enders, M.; Rudolph, R.; Pritzkow, H. *Chem. Ber.* **1996**, *129*, 459. (b) Foerstner, J.; Kettenbach, R.; Goddard, R.; Butenschön, H. *Chem. Ber.* **1996**, *129*, 319. (c) Siemeling, U. *Chem. Ber.* **1995**, *128*, 1135. (d) Siemeling, U.; Vorfeld, U.; Neumann, B.; Stammler, H.-G. *Chem. Ber.* **1995**, *128*, 481.

(21) Sterzo, C. L.; Miller, M. M.; Stille, J. K. *Organometallics* **1989**, *8*, 2331. (b) Sterzo, C. L.; Stille, J. K. *Organometallics* **1990**, *9*, 687.

(22) Barbeau, C.; Dichmann, K. S.; Ricard, L. *Can. J. Chem.* **1973**, *51*, 3027.

(23) March, Jerry *Advanced organic chemistry*; Wiley: New York, 1985; p 19.

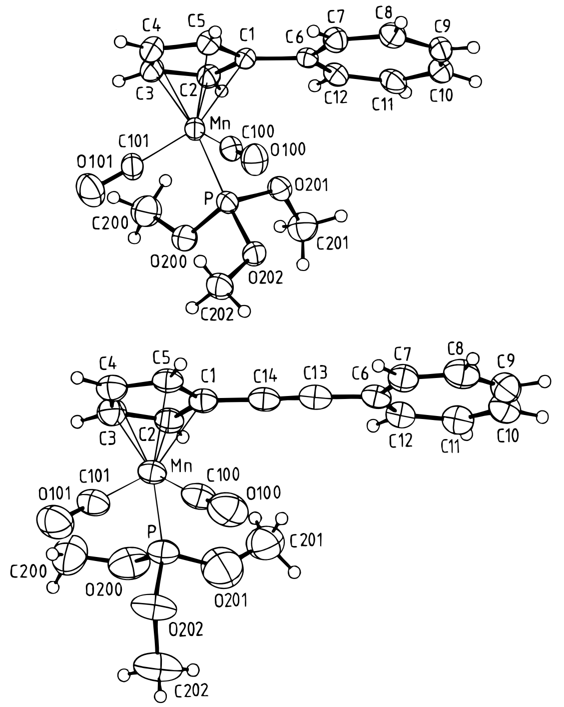

Figure 4. ORTEP drawings of the cations in **4b** (top) and **8b** (bottom).

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4b and 8b

	4b	**8b**
Mn−C100	1.771(7)	1.778(11)
Mn−C101	1.771(7)	1.756(10)
Mn−C1	2.144(6)	2.126(8)
Mn−C2	2.148(7)	2.152(8)
Mn−C3	2.155(7)	2.149(9)
Mn−C4	2.150(8)	2.131(9)
Mn−C5	2.138(7)	2.141(8)
Mn−P	2.179(3)	2.166(2)
C100−O100	1.154(7)	1.141(11)
C101−O101	1.148(7)	1.162(10)
C1−C2	1.428(9)	1.415(11)
C1−C5	1.425(10)	1.414(11)
C1−C6	1.467(8)	
C1−C14		1.431(14)
C2−C3	1.399(10)	1.426(12)
C3−C4	1.405(12)	1.406(12)
C4−C5	1.406(10)	1.400(13)
C6−C7	1.393(9)	1.372(12)
C6−C12	1.401(9)	1.390(12)
C6−C13		1.42(2)
C7−C8	1.376(9)	1.39(2)
C8−C9	1.387(10)	1.37(2)
C9−C10	1.352(11)	1.35(2)
C10−C11	1.386(10)	1.38(2)
C11−C12	1.373(9)	1.393(13)
C13−C14		1.200(14)
Mn−C100−O100	177.6(6)	176.6(10)
Mn−C101−O101	178.6(7)	177.8(9)
C100−Mn−C101	93.0(3)	91.2(5)
C100−Mn−P	92.2(2)	90.7(3)
C101−Mn−P	90.3(3)	89.0(3)
C1−C14−C13		178.7(9)
C6−C13−C14		176.7(9)

of CO, phosphites and phosphines have been studied[24] by means of X-ray crystallography[25] and IR,[26] NMR,[27] andphotoelectron spectroscopy,[28] and it is well accepted that the π-acceptor capabilities decrease in the order CO > $P(OR)_3$ > PR_3. This trend can be derived as well by comparison of the IR spectra of a consecutive series **a**, **b**, **c** of complexes **3**, **4**, **7**, and **8**, and the measured carbonyl stretching frequencies along with the calculated Cotton−Kraihanzel[29] CO force constants k(CO) are depicted in Table 3. Substitution of L = CO (**a**) by the weaker π-accepting ligands $P(OMe)_3$ (**b**) and PPh_3 (**c**) leads to enhanced Mn(dπ) → CO(π*) back-bonding to the remaining carbonyls and consequently lower k(CO)'s. Complexes **4** exhibit greater CO force constants when compared to the corresponding complexes **3** with identical $Mn(CO)_2L$ fragments, thus indicating that the sesquifulvalene ligand in **4** is a far better π-acceptor than the cyclopentadienyl ligand in **3** due to π-conjugation with the seven-membered tropylium ring. This also holds for complexes **7** and **8**, although the increase in k(CO) is much less pronounced.

Table 3. IR Data for Complexes 3, 4, 7, and 8 and UV/Vis Data and First Molecular Hyperpolarizabilities β of Sesquifulvalene Complexes 4 and 8

	$\tilde{\nu}$(CO), cm^{-1}		k(CO), N m^{-1}	λ_{max}, nm		$\Delta\tilde{\nu}$, cm^{-1}	β_{HRS}, 10^{-30} esu	
compd	A_1	E/B_1[a]		CH_2Cl_2	CH_3CN		CH_2Cl_2	CH_3CN
3a	2020	1933	1556					
4a	2035	1964	1597	536	506	1110	45	38
3b	1950	1889	1489					
4b	1964	1911	1517	612	581	870	54	53
3c	1930	1863	1453					
4c	1951	1900	1498	643	630	320	29	39
7a	2025	1938	1564					
8a	2030	1952	1581	537	491	1740	40	94
7b	1950	1885	1486					
8b	1956	1886	1491	649	583	1740	50	151
7c	1936	1872	1465					
8c	1941	1873	1470	740	650	1870	44	73

[a] E for $Mn(CO)_3$ complexes, B_1 for $Mn(CO)_2L$ complexes (L = $P(OMe)_3$, PPh_3).

Sesquifulvalene complexes **4** and **8** are intensely colored compounds. They show strong solvatochromic behavior and their ultraviolet visible spectra are markedly affected by varying the solvent, which usually is a good indication of possible NLO activity.[8,30] The lowest energy band λ_{max} (Table 3) is most strongly shifted upon changing the solvent from dichloromethane to acetonitrile ($\Delta\tilde{\nu}$ ranging from 320 cm^{-1} in **4c** to 1870 cm^{-1} in **8c**). Due to these hypsochromic shifts (negative solvatochromic behavior) we assign the lowest energy transition in these systems as being effectively the π to π* CT transition,[31] which is *approximately* (!) represented by the canonical forms **A** (ground state) and **B** (excited state) shown in Scheme 1 for **4** and Scheme 2 for **8**.

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[24] Huheey, J.; Keiter, E.; Keiter, R. *Anorganische Chemie*; de Gruyter: Berlin, New York, 1995; p 494 ff.

[25] (a) Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758. (b) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *J. Am. Chem. Soc.* **1969**, *91*, 4326.

[26] (a) Keiter, R. L.; Verkade, J. G. *Inorg. Chem.* **1969**, *8*, 2115. (b) Angelici, R. J.; Malone, M. *Inorg. Chem.* **1967**, *6*, 1731.

[27] (a) Wang, S. P.; Richmond, M. G.; Schwartz, M. *J. Am. Chem. Soc.* **1992**, *114*, 7595. (b) Buchner, W.; Schenk, W. A. *Inorg. Chem.* **1984**, *23*, 132. (c) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

[28] Bancroft, G. M.; Dignard-Bailey, L.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 3675.

[29] Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* 1962, *84*, 4432.

[30] (a) Paley, M. S.; Harris, J. M. *J. Org. Chem.* **1991**, *56*, 368. (b) Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bandy, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Nature* **1987**, *330*, 360.

[31] (a) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH Publishers: Weinheim, Germany, 1988. (c) Becker, H. G. O. *Einführung in die Photochemie*; Deutscher Verlag der Wissenschaften: Berlin, 1991.

Usually, extension of the conjugation path between an electron donor and acceptor does increase the polarizability significantly,[1,8] which is in agreement with the observation that complexes **8** generally exhibit greater solvatochromic behavior than complexes **4**.

As mentioned above, the color of the sesquifulvalene complexes strongly depends on the nature of the ligand L in the $Mn(CO)_2L$ fragment changing from red-purple in **4a**/**8a** to greenish-blue in **4b**/**8b** to deep blue in **4c**/**8c**. This represents an alternative spectrochemical series[32] in which significant bathochromic shifts (red shifts)[33] are observed for λ_{max} upon substitution of CO by the less π-accepting ligands trimethyl phosphite and triphenylphosphine (Table 3). Decreasing the π-acceptor capability of the ligand L leaves the metal fragment more electron rich thus increasing its donor strength, which reduces the energy difference between the two limiting resonance structures **A** and **B** (Schemes 1 and 2) or in other words decreases the HOMO/LUMO energy gap of the corresponding π to π^* CT excitation, respectively.[34]

The succesful tuning of the electronic and optical properties of **4a** and **8a**[7] encouraged us to measure the first molecular hyperpolarizabilities using the hyper Raleigh scattering technique.[13] The first molecular hyperpolarizabilities β of all sesquifulvalene complexes **4** and **8** were determined in dichloromethane and acetonitrile solutions using p-nitroaniline as external standard, and the results are shown in Table 3. The β values strongly depend on the solvent polarity, which is especially pronounced for complexes **8** exhibiting much greater solvatochromic behavior than complexes **4** (see above). These differences can be rationalized by resonance enhancement, which occurs when the frequency of the charge-transfer excitation is close to the frequency of the stimulating laser or close to the doubled frequency. However, it should be noted that in our case the simple two-level model[9] is not a versatile tool for the calculation of the static hyperpolarizability β_0 as the frequency-doubled scattered light is still in the region of very strong absorption. Furthermore, as expressed by eq 1, β_0 itself does depend on the solvent polarity and λ_{max} derived thereof.[35] Separation of resonance enhancement contributions and influences of solvent polarity would require the determination of β at a different basic laser wavelength.

The β values reported here are reasonably high compared to organic[36] and organometallic[8,34,37] compounds of comparable chromophore length. However, the heterobimetallic iron–chromium complexes reported by Heck et al.[8] exhibit significantly higher hyperpolarizabilities[38] indicating that complexation of the seven-membered tropylium ring by the $Cr(CO)_3$ fragment obviously induces an additional contribution due to ligand-to-metal charge transfer. This observation has to be taken into account for the future design of related NLO chromophores.

In summary, we have presented manganese(I) sesquifulvalene complexes as new NLO chromophores, whose electronic and optical properties can be easily and efficiently tuned by ligand substitution reactions. This concept could be extended to the introduction of readily available chiral phosphines leading to optically active compounds, which will crystallize in noncentrosymmetric space groups and thus fulfill a crucial requirement for the observation of macroscopic NLO effects.[39]

Experimental Section

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on a Bruker AM 250 (250 MHz) instrument. Infrared spectra were taken on a Perkin-Elmer 983 instrument. Elemental analyses (C, H, N) were performed at the Freie Universität Berlin on a Heraeus CHN-Rapid elemental analyzer. Mass spectra were recorded on a Varian MAT 711 instrument, and UV/vis spectra, on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer using 10^{-3} M solutions. Photochemical reactions were performed with a TQ 150 high-pressure mercury vapor lamp (Hanau). **3a**,[7] **4a**,[7] and **6**[22] were synthesized as previously described. Tropylium tetrafluoroborate was prepared by literature methods.[40] Triphenylcarbenium tetrafluoroborate, trimethyl phosphite, and triphenylphosphine were received from Aldrich and used without further purification.

Synthesis of 3b. A 500 mg (1.9 mmol) amount of **5** was dissolved in 10 mL of $P(OMe)_3$, and the mixture was heated at 120 °C for 60 min. Excess phosphite was removed *in vacuo*, and the yellow, oily residue was chromatographed on silica (4% H_2O) using hexane/dichloromethane (1:1) as eluent. **3b** was obtained as a yellow oil, 510 mg (70%). ^1H NMR ($CDCl_3$, 250 MHz): δ 6.64 (t, 2H, C_7 C*H*), 6.16 (dm, 2H, C_7 C*H*), 5.22 (m, 2H, C_7 C*H*), 4.58 (t, 2H, C_5 C*H*), 4.42 (t, 2H, C_5 C*H*), 3.55 (d, $^3J_{PC}$ = 12 Hz, 9H, POCH_3), 2.42 (t, 1H, C_7 C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.90 MHz): δ 229.8 (d, $^1J_{PC}$ = 39 Hz, *C*O), 130.9 (C_7 *C*H), 125.4 (C_7 *C*H), 124.3 (C_7 *C*H), 105.4 (C_5 *C*-1), 80.7 (C_5 *C*H), 80.2 (C_5 *C*H), 51.4 (PO*C*H_3), 38.0 (C_7 *C*-7). IR (CH_2Cl_2): ν(CO) 1950, 1889 cm^{-1}. MS (EI, 70 eV): *m/z* (relative intensity) 390 (30.5) [M^+], 359 (8.7) [$(M - OCH_3)^+$], 334 (60.9) [$(M - 2CO)^+$], 210 (100) [$(M - 2CO - P(OMe)_3)^+$], 155 (14.3) [$C_{12}H_{11}^+$]. Anal. Calcd for $C_{17}H_{20}MnO_5P$ (M_r = 390.25): C, 52.32; H, 5.17. Found: C, 52.67; H, 5.17.

Synthesis of 3c. A solution of **6** (2.48 g, 5.7 mmol) in 50 mL of thf was treated dropwise with *sec*-BuLi (4.5 mL of a 1.3 M solution in hexane, 5.9 mmol) at −78 °C. After the solution was stirred for 45 min at −78 °C, tropylium tetrafluoroborate (1.3 g, 7.3 mmol) was added as a solid and the reaction mixture was allowed to warm to room temperature. Stirring was continued for 60 min, and the solvent was removed *in vacuo*. Chromatography on silica (4% H_2O) with hexane/dichloromethane (1:1) yielded 2.57 g of a yellow solid, which according to its ^1H NMR spectra was an unseparable mixture

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(32) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1986.

(33) Note the alleged contradiction: In the order for instance from **4a** to **4c** λ_{max} is red shifted and consequently the color changes from red to blue.

(34) Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227.

(35) Stähelin, M.; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *191*, 245.

(36) (a) Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631. (b) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643.

(37) (a) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. (b) Yuan, Z.; Taylor, N. J.; Sun, Y.; Marder, T. B.; Williams, I. D.; L.-T.; Cheng *J. Organomet. Chem.* **1993**, *449*, 27. (c) Loucif-Saibi, R.; Delaire, J. A.; Bonazzola, L. *Chem. Phys.* **1992**, *167*, 369.

(38) For complex $\{CpFe[(\eta^5\text{-}C_5H_4)C\equiv C(\eta^7\text{-}C_7H_6)Cr(CO)_3\}BF_4$ incorporating the sesquifulvalene ligand **2**, $\beta = 570 \times 10^{-30}$ esu ($\beta_0 = 105 \times 10^{-30}$ esu) was reported.[8]

(39) (a) Dias, A. R.; Garcia, M. H.; Rodrigues, J. C.; Green, M. L. H.; Kuebler, S. M. *J. Organomet. Chem.* **1994**, *475*, 241.(b) Dias, A. R.; Garcia, M. H.; Robalo, M. P.; Green, M. L. H.; Lai, K. K.; Pulham, A. J.; Kuebler, S. M. *J. Organomet. Chem.* **1993**, *453*, 241. (c) Togni, A.; Rihs, A. *Organometallics* **1993**, *12*, 3368.

(40) Asao, T.; Oda, M. In *Methoden der Organischen Chemie (Houben-Weyl)*; Kropf, H., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1985; Vol. V/2c, p 49.

of **6** and **3c** (1:4.2). This mixture was used for subsequent hydride abstraction without further purification. Yield: 69% (based on **3c** in the product mixture). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.40 (m, 15H, PC_6H_5), 6.68 (m, 2H, C_7 C*H*), 6.19 (m, 2H, C_7 C*H*), 5.34 (m, 2H, C_7 C*H*), 4.41 (s br, 2H, C_5 C*H*), 4.05 (s br, 2H, C_5 C*H*), 2.45 (s br, 1H, C_7 C*H*). IR (CH_2Cl_2): ν(CO) 1930, 1863 cm^{-1}.

Synthesis of 4b. To a solution of **3b** (220 mg, 0.6 mmol) in 10 mL of CH_2Cl_2 was added triphenylcarbenium tetrafluoroborate (190 mg, 0.6 mmol) as a solid. The solution immediately turned green-blue, and stirring was continued for 60 min. After addition of 90 mL of diethyl ether the greenish-blue precipitate was isolated by filtration and washed with diethyl ether, 205 mg (75%): Mp 178−181 °C. ^{1}H NMR (CD_3CN, 250 MHz): δ 8.60 (m, 2H, C_7 C*H*), 8.44 (m, 4H, C_7 C*H*), 5.84 (t, 2H, C_5 C*H*), 5.30 (t, 2H, C_5 C*H*), 3.50 (d, $^3J_{PC} = 12$ Hz, 9H, POC*H*$_3$). ^{13}C NMR (CD_3CN, 62.90 MHz): δ 227.7 (d, $^2J_{PC} = 41$ Hz, *C*O), 169.6 (C_7 *C*-7), 150.6 (2 × C_7 *C*H), 147.6 (C_7 *C*H), 91.2 (C_5 *C*-1), 88.4 (C_5 *C*H), 88.1 (C_5 *C*H), 53.1 (d, $^2J_{PC} = 4$ Hz, PO*C*H$_3$). IR (CH_2Cl_2): ν(CO) 1964, 1911 cm^{-1}. MS (FAB): *m/z* (relative intensity) 389 (100) [M$^+$], 333 (28.7) [(M − 2CO)$^+$], 209 (28.2) [(M − 2CO − P(OMe)$_3$)$^+$]. UV/vis (CH_2Cl_2): ν (ϵ) 264 (21 000), 369 (20 800), 612 (9000) nm (L mol^{-1} cm^{-1}). UV/vis (CH_3CN): ν (ϵ) 261 (18 800), 361 (17 100), 581 (6700) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{17}H_{19}BF_4MnO_5P$ ($M_r = 476.05$): C, 42.89; H, 4.02. Found: C, 42.79; H, 4.35.

Synthesis of 4c. A mixture (1:4.2) of **6** and **3c** (1.38 g, 2.1 mmol of **3c**) was dissolved in 20 mL of CH_2Cl_2, and triphenylcarbenium tetrafluoroborate (700 mg, 2.1 mmol) was added as a solid. The solution immediately turned deep blue, and stirring was continued for 60 min. After addition of 100 mL of diethyl ether the blue precipitate was isolated by filtration and washed with diethyl ether, 980 mg (76%): Mp 209−212 °C. ^{1}H NMR (CD_3CN, 250 MHz): δ 8.37−8.10 (m, 6H, C_7 C*H*), 7.36 (m, 15H, PC_6H_5), 5.76 (t, 2H, C_5 C*H*), 5.10 (t, 2H, C_5 C*H*). ^{13}C NMR (CD_3CN, 62.90 MHz): δ 230.6 (d, $^2J_{PC} = 20$ Hz, *C*O), 169.5 (C_7 *C*-7), 150.4 (C_7 *C*H), 150.2 (C_7 *C*H), 146.9 (C_7 *C*H), 137.1 (d, $^1J_{PC} = 42$ Hz, P-*C*) 133.9 (d, $^2J_{PC} = 8$ Hz, P−C−*C*), 131.2 (P−C−C−C−*C*), 129.5 (d, $^3J_{PC} = 6$ Hz, P−C−C−*C*), 92.2 (C_5 *C*-1), 90.1 (C_5 *C*H), 88.4 (C_5 *C*H). IR (CH_2Cl_2): ν(CO) 1951, 1900 cm^{-1}. MS (FAB): *m/z* (relative intensity) 527 (15.3) [M$^+$], 471 (20.6) [(M − 2CO)$^+$], 154 (100) [$C_{12}H_{10}^+$]. UV/vis (CH_2Cl_2): ν (ϵ) 261 (27 600), 378 (21 000), 643 (7200) nm (L mol^{-1} cm^{-1}). UV/vis (CH_3CN): ν (ϵ) 258 (20 990), 373 (15 800), 630 (5020) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{32}H_{25}BF_4MnO_2P$ ($M_r = 614.26$): C, 62.57; H, 4.10. Found: C, 62.62; H, 5.13.

Synthesis of 5. **3a** (1.0 g, 3.4 mmol) dissolved in 200 mL of cyclohexane was irradiated in a photoreactor for 10 h. The solvent was removed *in vacuo*, and the brownish-yellow solid was purified by sublimation (0.01 mbar, 80 °C) and recrystallized from hexane to give **5** as yellow crystals, 550 mg (61%): Mp 148−151 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 6.70 (m, 2H, C_7 C*H*), 6.05 (t, 2H, C_7 C*H*), 4.57 (t, 2H, C_5 C*H*), 4.08 (t, 2H, C_5 C*H*), 3.53 (t, 2H, C_7 C*H*), 3.20 (t, 1H, C_7 C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.90 MHz): δ 235.3 (*C*O), 135.3 (C_7 *C*H), 135.0 (C_5 *C*-1), 131.2 (C_7 *C*H), 90.9 (C_5 *C*H), 80.6 (C_5 *C*H), 58.2 (C_7 *C*H), 33.4 (C_7 *C*-7). IR (cyclohexane): ν(CO) 1968, 1913 cm^{-1}. MS (EI, 70 eV): *m/z* (relative intensity) 266 (17.1) [M$^+$], 238 (5.3) [(M − CO)$^+$], 210 (100) [(M − 2CO)$^+$]. Anal. Calcd for $C_{14}H_{11}MnO_2$ ($M_r = 266.18$): C, 63.17; H, 4.17. Found: C, 63.33; H, 4.22.

Synthesis of 7b. **7a** (750 mg, 2.4 mmol) and 440 mg (0.42 mL, 3.5 mmol) of P(OMe)$_3$ dissolved in 250 mL of cyclohexane were irradiated in a photoreactor for 2 h. The solvent was removed *in vacuo*, and the crude product was purified chromatographically on silica (4% H_2O) with hexane/dichloromethane (2:1) as eluent. After removal of the solvent **7b** was obtained as a dark yellow oil, 280 mg (29%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 6.64 (t, 2H, C_7 C*H*), 6.14 (dm, 2H, C_7 C*H*), 5.30 (m, 2H, C_7 C*H*), 4.80 (t, 2H, C_5 C*H*), 4.45 (t, 2H, C_5 C*H*), 3.56 (d, $^3J_{PC} = 12$ Hz, 9H, POC*H*$_3$), 2.60 (t, 1H, C_7 C*H*). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 229.1 (d, $^2J_{PC} = 37$ Hz, *C*O), 131.0 (C_7 *C*H), 124.8 (C_7 *C*H), 123.0 (C_7 *C*H), 89.3 (*C*≡C), 86.0 (C_5 *C*-1), 85.4 (C_5 *C*H), 80.4 (C_5 *C*H), 74.6 (C≡*C*), 51.5 (PO*C*H$_3$), 32.1 (C_7 *C*-7). IR (CH_2Cl_2): ν(CO) 1950, 1885 cm^{-1}. MS (EI, 70 ev): *m/z* (relative intensity) 414 (21.7) [M$^+$], 358 (80.9) [(M − 2CO)$^+$], 234 (72.2) [(M − 2CO − P(OMe)$_3$)$^+$], 93 (100) [P(OMe)$_2^+$].

Synthesis of 7c. **7a** (1.00 g, 3.1 mmol) and PPh$_3$ (1.24 g, 4.71 mmol) dissolved in 220 mL of cyclohexane were irradiated in a photoreactor for 1 h (TLC control). The solvent was removed *in vacuo* from the brownish solution. The crude product was purified chromatographically on silica (4% H_2O) using hexane/dichloromethane (2:1) as eluent. After removal of the solvent **7c** was obtained as a yellow solid, 795 mg (46%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.43 (m, 15H, PC_6H_5), 6.66 (t, 2H, C_7 C*H*), 6.14 (dm, 2H, C_7 C*H*), 5.32 (m, 2H, C_7 C*H*), 4.50 (t, 2H, C_5 C*H*), 4.02 (t, 2H, C_5 C*H*), 2.53 (t, 1H, C_7 C*H*). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 232.1 (d, $^2J_{PC} = 25$ Hz, *C*O), 137.7 (d, $^1J_{PC} = 41$ Hz, P-*C*), 133.0 (d, $^2J_{PC} = 11$ Hz, P−C-*C*), 131.0 (C_7 *C*H), 129.5 (P−C−C−C−*C*), 128.1 (d, $^3J_{PC} = 10$ Hz, P−C−C−*C*), 124.7 (C_7 *C*H), 123.4 (C_7 *C*H), 89.9 (*C*≡C), 85.5 (C_5 *C*H), 82.5 (C_5 *C*H), 80.7 (C_5 *C*-1), 75.1 (C≡*C*), 32.3 (C_7 *C*-7). IR (CH_2Cl_2): ν(CO) 1936, 1872 cm^{-1}. MS (EI, 70 ev): *m/z* (relative intensity) 552 (10.0) [M$^+$], 496 (100) [(M − 2CO)$^+$], 262 (26.1) [PPh$_3^+$], 234 (29.1) [(M − 2CO − PPh$_3$)$^+$]. Anal. Calcd for $C_{34}H_{26}MnO_2P$ ($M_r = 552.49$): C, 73.92; H, 4.74. Found: C, 71.36; H, 5.05.

Synthesis of 8b. To a solution of **7b** (220 mg, 0.5 mmol) in 20 mL of CH_2Cl_2 was added triphenylcarbenium tetrafluoroborate (175 mg, 0.5 mmol) as a solid. The solution immediately turned blue, and stirring was continued for 30 min. After addition of 100 mL of diethyl ether the greenish-blue precipitate was isolated by filtration and washed with diethyl ether, 220 mg (83%): Mp 94−96 °C (dec). ^{1}H NMR (CD_3CN, 250 MHz): δ 8.78 (m, 6H, C_7 C*H*), 5.28 (t, 2H, C_5 C*H*), 4.88 (t, 2H, C_5 C*H*), 3.56 (d, $^3J_{PC} = 11$ Hz, 9H, POC*H*$_3$). ^{13}C NMR (CD_3CN, 62.90 MHz): δ 229.1 (d, $^2J_{PC} = 36$ Hz, *C*O), 154.8 (C_7 *C*H), 153.7 (C_7 *C*H), 153.0 (C_7 *C*H and C_7 *C*-7), 112.8 (C_5 *C*-1), 93.5 (*C*≡C), 90.7 (C_5 *C*H), 84.7 (C_5 *C*H), 72.1 (C≡*C*), 52.6 (PO*C*H$_3$). IR (CH_2Cl_2): ν(CO) 1956, 1886 cm^{-1}. MS (FAB): *m/z* (relative intensity) 413 (31.2) [M$^+$], 385 (27.8) [(M − CO)$^+$], 358 (20.1) [(M − 2CO)$^+$], 233 (19.2) [(M − 2CO − P(OMe)$_3$)$^+$], 178 (29.3) [$C_{14}H_{10}^+$], 93 (100) [P(OMe)$_2^+$]. UV/vis (CH_2Cl_2): ν (ϵ) 271 (14 000), 410 (12 400), 649 (5800) nm (L mol^{-1} cm^{-1}). UV/vis (CH_3CN): ν (ϵ) 266 (12 700), 392 (9700), 583 (4200) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{19}H_{19}BF_4MnO_5P$ ($M_r = 500.08$): C, 45.63; H, 3.83. Found: C, 45.60; H, 4.62.

Synthesis of 8c. To a solution of **7c** (600 mg, 1.1 mmol) in 20 mL of CH_2Cl_2 was added triphenylcarbenium tetrafluoroborate (360 mg, 1.1 mmol) as a solid. The solution immediately turned blue, and stirring was continued for 30 min. After addition of 100 mL of diethyl ether, a blue solid precipitated. Filtration and washing with diethyl ether yielded **8c** as a deep blue solid, 560 mg (80%): Mp 125 °C (dec). ^{1}H NMR (CD_3CN, 250 MHz): δ 8.76 (m, 4H, C_7 C*H*), 8.60 (m, 2H, C_7 C*H*), 7.44 (m, 15H, PC_6H_5), 5.12 (t, 2H, C_5 C*H*), 4.80 (t, 2H, C_5 C*H*). ^{13}C NMR (CD_3CN, 62.90 MHz): δ 233.3 (d, $^2J_{PC} = 24$ Hz, *C*O), 154.7 (C_7 *C*H), 153.5 (C_7 *C*H), 152.9 (C_7 *C*-7), 152.5 (C_7 *C*H), 135.9 (s br, P-*C*), 133.7 (s br, P−C−*C*), 131.2 (s br, P−C−C−C−*C*), 129.3 (s br, P−C−C−*C*), 114.1 (C_5 *C*-1), 94.7 (*C*≡C), 91.5 (C_5 *C*H), 86.9 (C_5 *C*H), 73.5 (C≡*C*). IR (CH_2Cl_2): ν(CO) 1941, 1873 cm^{-1}. MS (FAB): *m/z* (relative intensity) 551 (5.7) [M$^+$], 495 (10.9) [(M − 2CO)$^+$]. UV/vis (CH_2Cl_2): ν (ϵ) 425 (13 900), 740 (4700) nm (L mol^{-1} cm^{-1}). UV/vis (CH_3CN): ν (ϵ) 405 (13 200), 650 (4200) nm (L mol^{-1} cm^{-1}). Anal. Calcd for $C_{34}H_{25}BF_4MnO_2P$ ($M_r = 638.29$): C, 63.98; H, 3.95. Found: C, 63.69; H, 4.56.

X-ray Structural Determination of 4b, 5, and 8b. Single crystals are stable under ambient conditions and were mounted on glass pins for data collection (room temperature, Enraf-Nonius Turbo-CAD4 single-crystal diffractometer, rotating anode generator, Cu Kα radiation, ω-scan mode). Unit cell dimensions were determined from the angular setting of 25

Table 4. Crystallographic Data for 4b, 5, and 8b

	4b	**5**	**8b**
cryst size, mm	0.65 × 0.04 × 0.02	0.40 × 0.35 × 0.07	0.20 × 0.15 × 0.05
formula	$C_{17}H_{19}BF_4MnO_5$	$C_{14}H_{11}MnO_2$	$C_{19}H_{19}BF_4MnO_5P$
fw	476.04	266.17	500.07
wavelength, Å	1.54176	1.54176	1.54176
cryst system	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$ (No. 2)	*Pnma* (No. 62)	$P2_1/c$ (No. 14)
a, Å	6.686(2)	6.455(1)	10.9676(7)
b, Å	8.761(3)	11.911(2)	12.918(1)
c, Å	17.276(8)	14.653(1)	15.600(1)
α, deg	84.36(11)		
β, deg	88.09(6)		93.50(2)
γ, deg	86.23(8)		
V, Å^3	1004.5(7)	1126.6(3)	2206.0(3)
Z	2	4	4
ρ_{calc}, g/cm^3	1.574	1.569	1.509
μ, mm^{-1}	6.685	9.400	6.121
$F(000)$	484	544	1020
θ range, deg	$2.57 \leq \theta \leq 60.05$	$4.78 \leq \theta \leq 59.84$	$4.04 \leq \theta \leq 59.97$
index ranges	$0 \leq h \leq 7$	$0 \leq h \leq 7$	$-12 \leq h \leq 12$
	$-9 \leq k \leq 9$	$0 \leq k \leq 13$	$-1 \leq k \leq 14$
	$-19 \leq l \leq 19$	$-16 \leq l \leq 16$	$-17 \leq l \leq 2$
T_{min}, T_{max}	0.890, 0.999	0.728, 0.995	0.738, 0.996
rflns collcd	3278	1729	4376
independent rflns	2983 [R(int) = 0.0329]	884 [R(int) = 0.0226]	3279 [R(int) = 0.0373]
no. of params	314	105	293
GOF on F^2	1.027	1.071	1.031
R [$I > 2\sigma(I)$]	0.0649	0.0393	0.0820
wR2 (all data)	0.1821	0.1064	0.2654
Δ/σ (max)	<0.001	<0.001	0.006
largest diff peak and hole, e/Å^3	0.688 and −0.426	0.447 and −0.524	0.803 and −0.596

reflections. Crystal data are given in Table 4. Semi-empirical absorption correction (ψ-scan) was applied. Structures were solved with direct methods (SHELXS 86)[41] and refined with standard methods (refinement against F^2 with SHELXL 93).[42] For **4b** and **5**, hydrogen atoms were refined isotropically, except for the methyl groups in **4b**, which were refined in the riding model (SHELXL 93).[42] In **8b** all hydrogen atoms were refined in the riding model. In **4b** and **8b**, the fluorine atoms in the tetrafluoroborate anions exhibit very high displacement parameters probably indicating excessive thermal motion or disorder, which is not resolved. Crystals of **8b** showed reduced diffraction power compared to **4b** and **5** resulting in a higher R value and larger standard deviations obtained in the refinement.

Hyper Raleigh Scattering. The experiments were performed at a wavelength of 1064 nm with a mode-locked Q-switch Nd:YAG laser (Quantronix 5216). Solutions of p-nitroaniline in acetonitrile and dichloromethane were used as external reference ($\beta(CH_2Cl_2) = 16.9 \times 10^{-30}$ esu, $\beta(CH_3CN) = 29.2 \times 10^{-30}$ esu).[35] The general experimental setup is described in ref 13b. Further experimental details will be published elsewhere.[43]

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Supporting Information Available: Tables of X-ray data, positional and thermal parameters, and bond distances and angles (24 pages). Ordering information is given on any current masthead page.

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(41) Sheldrick, G. M. *SHELXS 86, Program for the Solution of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1986.

(42) Sheldrick, G. M. *SHELXL 93, Program for the Refinement of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1993.

(43) Jentzsch, T.; Werncke, W.; Tamm, M. Manuscript in preparation.