η^1 and η^2 complexes of λ^3-1,2,4,6-thiatriazinyls with $CpCr(CO)_x$ {x = 2,3}

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Supplementary material

B3PW91/6-31G+(d) calculations

The structures of diamagnetic adducts were optimized in their ground states using density functional theory in the GAUSSIAN 98W suite of programs.[1] The B3PW91 functional[2] with the 1991 gradient-corrected correlation functional of Perdew and Wang[3] was used; this hybrid functional has previously been shown to provide realistic geometries for organochromium complexes.[4] The Gaussian basis set 6-31+G(d) was used for geometry optimization and final energy calculations. The optimized geometry obtained at the B3PW91/6-31+g(d) level of theory for the model compound of **5** is shown in Figure S1. The calculations clearly demonstrate an interaction of the erstwhile π_4 SOMO of the TTA radical with one of the "T_{2g}" set of three bonding metal *d* orbitals. This is the only net bonding interaction of the ligand with the metal. Note that it is this same orbital that is

postulated to form the main "transannular" bond in dimers of the neutral thiatriazinyls such as $[\mathbf{4}]_2$.[5]

We have also performed B3PW91/6-31+g(d) calculations on a model of **14** using the same 3,5-dihydro thiatriazinyl ligand as employed in the model calculations for **5**. The optimized geometry is shown in Figure S2. The bonding interactions for this system are fully compatible with a 3e donor model for the ligand, and resemble those in the 1,2,3,5-dithiadiazoyl complexes with the same metal fragment **1** and **2**.[6]

References

[1] Gaussian 98W, Revision A.9, M. J. Frisch, *et al.* Gaussian, Inc., Pittsburg, PA, 1998.
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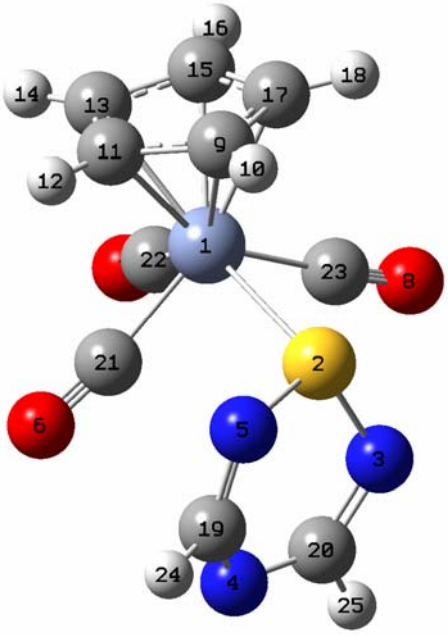
[3] J. P. Perdew, Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.
[4] C. N. Carlson, J. D. Smith, T. P. Hanusa, W. W. Brennessel, V. G. Young, Jr., *J. Organomet. Chem.* 2003, **683**, 191.
[5] R. T. Boeré, A. W. Cordes, P. J. Hayes, R. T. Oakley, R. W. Reed, W. T. Pennington, *Inorg. Chem.*, 1986, **25**, 2445
[6] H. F. Lau, V. W. L. Ng, L. L. Koh, G. K. Tan, L. Y. Goh, T. L. Roemmele, S. D. Seagrave and R. T. Boeré, *Angew. Chem.*, 2006, **118**, 4610; *Angew. Chem. Int. Ed.*, 2006, **45**, 4498.

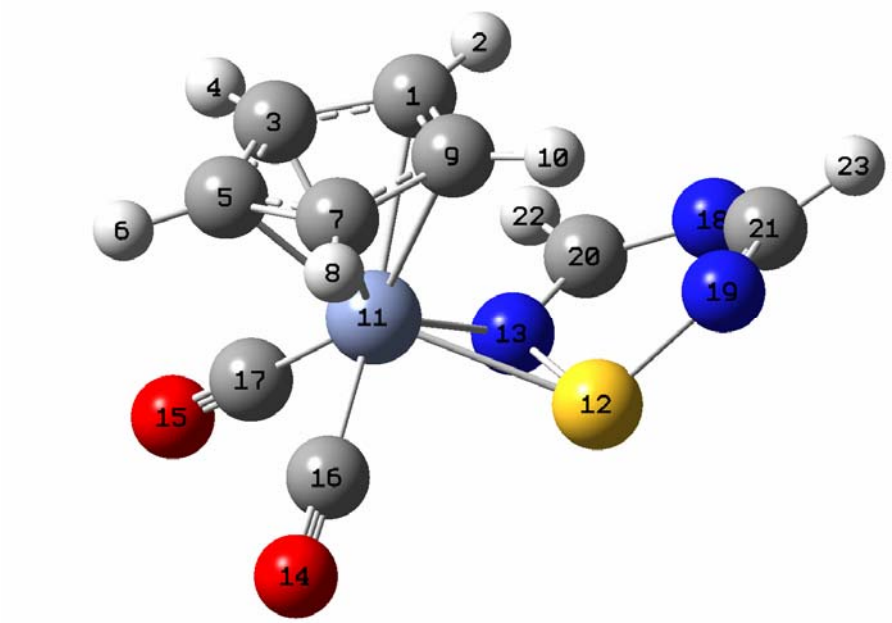
B3PW91/6-31G+(d) calculations

Figure S1 **$CpCr(CO)_3\{\eta^1\text{-}SN_3(CH)_2\}$** -2217.3 631166 Hartree



Center Number	Atom Type	Coordinates (Angstroms) X	Y	Z
1	Cr	0.871228	0.03339	0.056854
2	S	-1.27686	-0.46115	-1.10309
3	N	-2.18504	0.923895	-1.18482
4	N	-3.35002	0.254862	0.795534
5	N	-2.20827	-1.5802	-0.27441
6	O	-0.81014	-0.35361	2.536148
7	O	1.825595	2.324514	1.739789
8	O	0.505513	2.475034	-1.67652
9	C	1.310921	-1.8876	-0.93753
10	H	0.656839	-2.45558	-1.41782
11	C	1.65647	-2.0006	0.406728
12	H	1.29009	-2.6625	1.047148
13	C	2.64471	-1.07039	0.678068
14	H	3.12737	-0.96509	1.536223
15	C	2.913586	-0.37419	-0.51176
16	H	3.62677	0.299954	-0.64583
17	C	2.08022	-0.89074	-1.49663
18	H	2.087439	-0.63379	-2.45467
19	C	-3.09919	-1.06303	0.544512
20	C	-2.97745	1.141476	-0.14552
21	C	-0.24934	-0.18333	1.565043
22	C	1.464649	1.437955	1.121674
23	C	0.578143	1.536904	-1.03713
24	H	-3.75324	-1.75772	1.028787
25	H	-3.4158	2.115569	-0.08312

Figure S2 $CpCr(CO)_2\{\eta^2\text{-}SN_3(CH)_2\}$
Endo isomer: -2104.1323372 Hartree



Center Number	Atom Type	Coordinates (Angstroms) X	Y	Z
1	C	-0.0483	1.953868	0.777423
2	H	-0.97229	2.070616	1.330516
3	C	1.222161	1.638447	1.334405
4	H	1.444836	1.520383	2.387672
5	C	2.161484	1.55683	0.260671
6	H	3.222346	1.360238	0.353705
7	C	1.453666	1.796787	-0.95175
8	H	1.879214	1.80931	-1.94753
9	C	0.092012	2.047926	-0.62546
10	H	-0.71172	2.229799	-1.3291
11	Cr	0.709916	-0.00674	0.013177
12	S	-1.24632	-0.8751	-1.04099
13	N	-1.0074	-0.91184	0.645307
14	O	2.335833	-1.54554	-1.98277
15	O	2.117212	-1.85925	1.920784
16	C	1.687495	-0.97105	-1.21294
17	C	1.566973	-1.1612	1.181852
18	N	-3.28811	-0.2879	0.990083
19	N	-2.51319	0.26001	-1.26034
20	C	-2.07783	-0.65302	1.392229
21	C	-3.35304	0.264939	-0.26058
22	H	-1.90836	-0.72827	2.46914
23	H	-4.24212	0.876434	-0.42939